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DIFFUSION COATING PROCESS FOR COLUMBIUM BASE ALLOYS

TECHNICAL DOCUMENTARY REPORT No. ML-TDR-64-71

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
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FORWORD

This report was prepared by Chance Vought Corporation as Report No. 00.122 under USAF Contract No. AF 33(616)-7596. This contract was initiated under Project No. 7361, "Materials Applications," Task No. 738102, "Materials Preproduction Processes." The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with L. N. Hjelm, 1/Lt, USAF, acting as Project Engineer.

This report covers work conducted from February 1961 to February 1962.

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ABSTRACT

This program was to improve and optimize coatings for columbium alloys, protective in air to 2600°F for at least 10 hours. Process variables of two different silicide base coating systems (Si-Cr-Al and Si-Cr-B) applied by a two-step pack cementation process were optimized by statistical methods. Coatings were evaluated on D-31, C-103, Cb-1Zr (FS-80), and FS-82 columbium alloys.

Oxidation resistance testing included furnace testing in moving air, sustained load thermal cycling, propane torch and ram-jet tests. Tensile strength and bend properties of uncoated and coated alloys were evaluated at room and elevated temperatures. An analytical evaluation of these systems was conducted to characterize the coating components. In addition, oxidation tests in the range 1000° to 2000°F were conducted to determine "di-silicide pest" effects on the two systems. The Si-Cr-B system was unaffected by this phenomenon.

A simulated leading edge assembly containing welds and rivets in exposed locations was fabricated, coated with the Si-Cr-B system, and tested in glide re-entry conditions. There was no visible detrimental effect on the coating as a result of this test.

This technical documentary report has been reviewed and is approved.

W. P. Conrady

W. P. CONRADY, Chief
Materials Engineering Branch
Materials Applications Division

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INTRODUCTION

This report covers the accomplishments in a program for the development and optimization of a diffusion coating process for columbium base alloys for high temperature oxidation protection. In particular, this work was directed toward the improvement of reliability and reproducibility of a pack cementation process for diffusion coating of columbium sheet material.

The requirement for this program stemmed from Air Force recognition that advanced technology will require completely reliable coated refractory alloys for structural and heat shield applications at high temperatures. Pack cementation diffusion coatings to protect the base metal from oxidation at temperatures to 2600°F are a means of satisfying this requirement.

Although a number of coatings for refractory metals have been developed using the pack cementation process, they have usually been realized through "trial and error" techniques without a thorough investigation of the many variables. This program has been an integrated sequence of study, development, and testing to accomplish the optimization of the coating system and the required processing techniques to provide columbium alloys with oxidation resistance to temperatures as high as 2600°F.

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SCOPE OF PROGRAM

The purpose of the program was to extend the development of pack cementation or "diffusion coatings" for columbium base sheet alloys to the point of coating optimization, reliability, and reproducibility required for Air Force use.

Phase I of the program included a survey of available literature and a review of process and material variables with respect to their effect on coating integrity and oxidation resistance. The analysis of available data was focused on requirements for severe service to 2600°F.

The more promising systems developed by Ycught, modified by information gained in the foregoing survey, were then evaluated in preliminary tests designed to give the following information:

1. Comparable life
2. Coating ductility
3. Thermal shock resistance
4. Base metal characteristics
5. Base and coating thicknesses
6. Adhesion
7. Coating microstructure
8. Change in strength due to coating
9. Emissivity
10. Melting points

The tests in Phase I were conducted on three 0.020" thick columbium alloys, Wah Chang Cb-1 Zr, Wah Chang C-103, and duPont D-31. The chemical analysis of these alloys is given in Table I. The tests included the following:

1. Oxidation resistance of specimens coated with ten promising coatings.
2. Tensile tests at room temperature on coated and uncoated specimens.
3. Tensile tests at 2500°F on coated specimens.
4. Thermal cycle tests on coated specimens under sustained load.
5. Bend tests on coated and uncoated specimens at room temperature and -100°F.
6. Metallcgraphic examination.

On the basis of the above tests, two ccatings (Si-Cr-Al and Si-Cr-B) were selected for further optimization.

Phase II consisted of evaluation of process variables involved in producing the two ccatings. A single alloy, Cb-1 Zr, was used to establish the effect of each variable on the finished coating and substrate. The variables evaluated for optimization were the following:

1. Coating deposition temperature
2. Coating deposition time
3. Retort seal permeability
4. Pack density
5. Pack mix particle size
6. Pack composition

The effect of these variables on deposited coatings was evaluated by means of oxidation tests at 2600°F in moving air, and by oxidation tests at 2000°F on coated specimens which were elongated by bending. Metallographic examination was made of base metal, interfaces, and complete coating.

In order to more fully characterize the coatings produced during the Phase II evaluation, a coating composition study was conducted by combined X-ray diffraction, chemical analysis, and metallographic techniques. The results of these studies are given in this report.

Work in Phase III was divided into three parts as follows: (1) determination of process reliability and reproducibility by coating and testing three identical sets of specimens, (2) selection of the best techniques for coating complex multi-component assemblies, and (3) delivery of coated test specimens and test assembly to ASD.

In order to determine process reliability and reproducibility, three identical sets of test specimens were coated and tested as shown below:

<u>Alloy</u>	<u>Coating System</u>	<u>Test</u>
D-31	Si-Cr-Al	3 Oxidations 2 Bend elongations
D-31	Si-Cr-B	3 Oxidations 2 Bend elongations
C-103	Si-Cr-Bl	3 Oxidations 2 Bend elongations
C-103	Si-Cr-B	3 Oxidations 2 Bend elongations
Cb-1 Zr	Si-Cr-Al	3 Oxidations 2 Bend elongations
Cb-1 Zr	Si-Cr-B	3 Oxidations 2 Bend elongations

Techniques for coating complex multi-component assemblies were evaluated by preparation and testing of representative specimens fabricated in the form of bolts, rivets, skin sections, welds and structural stiffeners and their subsequent assemblies. Coatings were deposited on riveted specimens which were fabricated by the following methods: (1) assembly after coating with a subsequent

final coat, (2) complete assembly prior to coating, (3) coating before sub-assembly, then final assembly followed by a subsequent final coating.

Delivery of coated test specimens and test assembly to ASD included 24 coated specimens for additional tests.

LITERATURE SURVEY

A literature survey was conducted at the start of the program to determine oxidation characteristics and mechanical properties of columbium alloys, as well as the state-of-the-art of coatings for oxidation protection.

Oxidation of bare columbium proceeds in two ways: (1) reaction with the metal to form the oxide, and (2) contamination of the surface of the un-reacted metal to form a solid solution of oxygen and nitrogen in the metal. Such contamination of the metal with oxygen results in surface and sub-surface embrittlement or hardening, Ref. 1.

A number of factors other than time and temperature affect the oxidation of a metallic or inter-metallic surface. Among these factors are the condition of the surface and the surface area of the metal, composition and pressure of the gas, orientation and structure of the metal-oxide crystals formed, and the ratio of the volumes of the metal-oxides and the underlying metal.

The rate of oxidation as well as some of the physical properties of the formed metal-oxide are determined by the orientation of the grains of the metal-oxide crystals formed, Ref. 2. The ratio of the specific volume of the oxide to that of the metal appears to be related to the structure and protective effect of the metal oxide. For example, if the ratio of specific volumes is very small, the structure of the oxide is generally porous, crumbly and unsuitable for oxidation protection.

A review of available literature on the effects of various elements on oxidation resistance of columbium revealed the following:

1. Molybdenum.-- Molybdenum additions as an alloying agent in columbium improves its oxidation behavior until the solubility of molybdenum in the oxide scale is exceeded, above 7.5 atomic per cent of molybdenum, at which point catastrophic oxidation occurs, Ref. 3.

2. Vanadium.-- Vanadium provides some protection, as does molybdenum, up to 12.5 atomic per cent vanadium in the columbium surface coating, Ref. 3.

3. Titanium.-- Twenty and higher atomic percent of titanium considerably improves the oxidation resistance of columbium through formation of double oxides (Cb_2O_5 TiO_2 and $3\text{Cb}_2\text{O}_5$ TiO_2). This element effectively "getters" the inward-diffusing oxygen and precipitates oxides to form an internal scale, Ref. 3 and 4.

4. Zirconium.-- Zirconium offers relatively poor oxidation resistance at concentrations below 50 atomic per cent. Above 50 atomic per cent zirconium in columbium improves the oxidation resistance by the formation of a complex oxide scale - Cb_2O_5 ZrO_2 , Ref. 3.

5. Chromium.-- It is believed that the presence of Cr_2O_3 as a second oxide combines with the Cb_2O_5 to form a more refractory oxidation resistant scale, Ref. 3.

6. Aluminum.-- Aluminum increases the oxidation resistance of columbium in a manner similar to titanium. When added along with chromium it effectively improves the resistance to inward diffusing oxygen.

7. Silicon.-- Silicon substantially increases the oxidation resistance of columbium alloys through the formation of columbium silicide which on contact with high temperature oxidation forms a protective coating of SiO_2 .

Alloying of columbium has resulted in oxidation resistance approximately 50 times better than unalloyed columbium. However, even the most oxidation resistant alloy reported would require some form of protective coating for prolonged elevated temperature applications in oxidizing environments, Ref. 1.

Columbium alloys commercially available in sheet form were found to be limited because of rolling and fabrication difficulties. None of the sheet materials available were found which fully satisfied the requirements of fabricability, oxidation resistance, and high temperature strength. Data available from the literature on typical commercial alloys are shown in Table 2, Ref. 4.

Considering the requirements a coating for protecting columbium must meet, careful selection of coating materials capable of withstanding re-entry conditions is mandatory. For long duration oxidation resistance, coatings formulated around inter-metallics which form protective oxide films upon exposure to high temperature oxidation warrant the most attention. The silicides and such elements as Cr, Al, Ti, etc. form protective metal oxide films upon exposure, Ref. 5.

Methods which have been used in attempts to develop satisfactory coatings for columbium have included the following:

- Electro-Deposition Coatings
- High Temperature Sprayed Coatings
- Dip Coatings
- Clad Coatings
- Vapor Deposition Coatings
- Pack Cementation Coatings

1. Electro-Deposition Coatings.-- Electroplated coatings on columbium have shown a tendency to poor adhesion, peeling, and/or formation of brittle inter-metallics, Ref. 5. Platings of chromium, copper, iron, gold, nickel, and platinum have been made on columbium, Ref. 6 and 7.

Work by General Electric indicated that Fanssteel 82 could be protected by a 2 mil chromium coating for one hour at 2500°F, however, the plating was very brittle after oxidation testing, Ref. 8. None of these electroplated coatings offered a satisfactory combination of oxidation resistance and base metal strength characteristics, Ref. 6 and 8.

In general, electroplated coatings are limited in application by the "throwing power" of the electroplating solutions and the ingenuity used in racking and placing anodes. It is difficult to provide essential coating encapsulation on many shapes and for this reason this method in application is not considered a versatile approach.

Coatings are being successfully applied to refractory metals by the use of electrophoresis, Ref. 9, 10 and 11. They are principally limited at present to small components. The main advantages of using an electrophoresis technique are its excellent throwing power, and the fact that oxidation resistant non-conductive materials can be readily applied to the substrate.

2. High Temperature Sprayed Coatings.-- Literature reveals that more work has been reported on spray coatings for oxidation protection than any other method. Most of the materials used in these evaluations were originally developed for protection of molybdenum. A composition of chromium-34 weight % silicon-20 weight % aluminum withstood six hours at 2500°F. Reproducibility was not good since later tests were unable to withstand over two hours at this temperature, Ref. 12. A duplex sprayed coating consisting of a 4 mil coating of a proprietary material overlaid with a 4 mil coating of a modified molybdenum disilicide is reported to be oxidation resistant to 2700°F, Ref. 13.

A wide variety of flame sprayed coatings, representative of sprayed coatings, have been developed by Vought, Ref. 14, 15, 16, 17, and 18. Although they are not alone suitable as oxidation resistant coatings they provide thermal barriers for specific conditions.

For purposes of protecting thin material or large skins this method has the following limitations:

- Not adaptable to thin sheet edges
- Limited to simple shapes
- Localized heating may cause distortion and warping
- Excessive weight required because of marginal porosity

3. Dip Coatings.-- Considerable initial success has been obtained by hot dipped coatings, particularly when they are given a supplementary diffusion treatment. Zinc has been applied to columbium by a hot dip and diffusion technique to provide an oxidation resistant coating, Ref. 19. In its simplest form, this new coating consists of layers of inter-metallic zinc-columbium compounds on the surface of the columbium. The upper limit of this coating for sustained use appears to be 2050°F at which point the columbium-zinc inter-metallic compound has an excessive vapor pressure which tends to rupture the coating, Ref. 20 and 27.

Dipping of columbium and coated columbium in molten aluminum has effectively improved the oxidation resistance of columbium at temperatures of 2500°F for short time periods, Ref. 15. This property probably results from the inter-diffusion of aluminum into the columbium surface forming an alloy which on oxidation yields a protective Al_2O_3 type scale.

Numerous aluminum alloy combinations containing from 2-15 weight % silicon and from 6-15 weight % chromium have been applied to columbium by hot dipping. These have been evaluated by General Electric, Ref. 21. The aluminum-10 weight % chromium-2 weight % silicon alloy was the most effective, and is reported to have protected Fansteel 82 for more than two hours at 2500°F, Ref. 5 and 22.

A coating of aluminum-11 weight % silicon applied by a slurry dipping technique and post-baking at 2000°F in argon is reported to prevent oxidation of the substrate for two hours at 2500°F with no visible oxidation, Ref. 14. Coatings have also been successfully applied to columbium by use of various ceramic frit compositions. These coatings appear to be subject to limitations both during processing and by their inability to protect substrate edges and corners, Ref. 23.

4. Clad Coatings.--Clad coatings of thin stainless steel have been made on columbium, Ref. 24. In general, no successful columbium-base clad materials suitable as a structural component for high temperature use in an oxidizing environment have been developed, Ref. 3 and 5. It should also be noted that this protection method suffers from the inherent difficulty of protecting edges and recesses, Ref. 5.

5. Vapor Deposition Coatings.--Vapor deposited coatings of silicon on columbium are reported by Fansteel Corporation to have given oxidation protection for 10 hours at 1800°F, Ref. 25. Coatings of nitrides, carbides, borides and silicides have also been deposited on pure columbium by vapor deposition. The oxidation resistance characteristics of these coatings on columbium appears to be good to approximately 2000°F, although no specific tests were noted, Ref. 26.

Thompson-Ramo-Wooldridge has recently completed a systematic investigation on the effects of process variables on their (Cr-Ti)-Si coating on unalloyed columbium, D-31 alloy, and F-48 alloy. They found for their process the optimum coating consisted of a Cr-50 Ti layer about 1 mil thick (applied by vacuum distillation at 2350°F) overlaid with about .1 mil of silicon (applied by vacuum distillation at 2200°F). Columbium, D-31, and F-48 were protected in cyclic oxidation at 2500°F for 12, 24 and 20 hours, respectively. The coating life decreased with increasing temperature and at 2800°F, the coating protected D-31 for one hour. Coatings of aluminum and of aluminum modifications of Cr-Ti-Si were also under evaluation and were protective to D-31 in cyclic oxidation at 2300°F and 2500°F, Ref. 27 and 28.

6. Pack Cementation Coatings.--The pack cementation process consists of basically two steps (1) deposition, and (2) diffusion which involves reduction, ion exchange, the formation of solid solutions and/or intermetallic compounds. The two steps may be conducted simultaneously during processing, or the diffusion cycle may be introduced as a separate step.

Diffusion coatings applied by use of the pack cementation process appear to provide the most promise of meeting the requirements of a satisfactory coating for protection against high temperature oxidation, Ref. 19, 20, 29 and 30.

GENERAL COATING PROCEDURE

Specimen blanks were sheared from sheet stock to the desired size and machined or hand finished to meet the desired requirements. All edges and corners were rounded to a smooth, continuous radius. Specimen sizes and dimensions used in the program are shown in Figures 1 and 2.

The specimens were cleaned, air dried, and oven heated immediately prior to loading the retort. All specimens, after cleaning, were handled with clean lint-free gloves or clean instruments.

The pack material components were carefully weighed and mixed in a suitable laboratory blender. The blender was allowed to operate for a minimum of one hour to insure a uniform blend of the pack materials.

The clean, dry specimens were placed in a retort half filled with the pack material for the initial silicide coating, Figure 3. Additional pack material was used to fill the retort. The cover was placed on the retort, and the seal filled with sand or other sealing material.

The loaded retort was then placed in a furnace capable of maintaining $\pm 25^{\circ}\text{F}$ temperature control in the range from 1700°F to 2300°F , Figure 4. After the retort was in the furnace for the desired period of time, it was removed and allowed to cool in air. When the retort had cooled to approximately 140°F , it was unloaded. The specimens were washed, dried, and held for subsequent coating or evaluation.

The second coating was applied in a retort in the similar manner as the initial silicide coat.

TEST PROCEDURES

1. Oxidation Resistance Tests.-- One of the primary considerations in this program was the ability of a coating to protect columbium and columbium alloys from oxidation at 2600°F. Oxidation resistance afforded by the coating was determined in this program on the basis of visual and metallographic inspection and weight variations.

In order to insure oxidizing conditions, coated specimens were exposed in a laboratory furnace in which air, or an oxygen-nitrogen mixture, was allowed to flow over the test specimens at a controlled flow rate, Figure 5. This flow rate was controlled to allow a linear flow rate of one foot per second over the specimens during test, or a complete change of air every three seconds.

Measurement of specimen temperature during exposure was made with a Leeds and Northrop Optical Pyrometer Catalog No. 8622. Temperature control was maintained with a Honeywell Brown Pyr-O-Vane controller capable of controlling to 3000°F with a platinum-platinum 13% rhodium thermocouple mounted in the furnace hot zone.

Unless otherwise noted, specimens were run and tested in duplicate. The average exposure to failure is reported in the average of the exposure time for the two specimens. Coated specimens were weighed before and after each one hour exposure in the furnace. The specimens were carefully examined after each exposure for evidence of oxidation and coating failure.

2. Room and Elevated Temperature Tensile Strength.-- Room temperature tensile strength tests on coated and uncoated specimens were conducted on tensile specimens prepared as shown in Figure 1. Tensile tests were conducted in accordance with ASTM Specification E-8-57T "Tentative Methods of Tension Testing of Metallic Materials". Tests were conducted on a Baldwin Universal Tester.

Elevated temperature tensile tests on coated specimens were also conducted in accordance with the ASTM specification. The coated specimens were heated in air to the desired temperature by quartz lamp radiant heaters while the specimens were mounted in the Baldwin tester. Temperature of the specimens during test was monitored by use of platinum-platinum 13% rhodium thermocouples mounted on the specimen. The specimens were heated to the desired temperature and allowed to stabilize for five minutes before being loaded in test.

3. Load Cycle Test.-- This test was designed to determine the effect of static loads on coated specimens which are alternately heated and cooled. It was performed by placing a coated specimen under a static load and heating in air by quartz lamp radiant heaters. The stress level was determined by the mechanical properties of the coated alloy, as determined by the elevated temperature tensile tests described above.

The specimens were thermally cycled by heating in five minutes to 2500°F, holding for five minutes at that temperature, and cooling to room

temperature in five minutes. The thermal cycle was controlled by a Research Incorporated ignition power controller coupled with an automatic time-temperature programmer. Each specimen was cycled until failure. Observations were made after each cycle for visible oxidation or changes in the coating.

4. Transition Temperature Bend Test.-- It was desirable to determine the effect of the coating and coating process on the ductility of thin sheet. A bend test appeared to be the best method for determining this characteristic since it would provide data on the effects of tension and compression. In addition it provides an indication of the influence of the coating on the base metal ductile-brittle transition temperature.

The more common bend test fixtures were unsatisfactory because they involved bending a specimen over a mandrel. Such a mandrel obscures visual inspection of the compression side of the test specimen during the test. The mandrel would also effect a coating because of high localized bearing loads.

A test fixture was designed and constructed which was capable of bending a 1" x 4" specimen through 180° with a decrease in bend radius, without the use of a mandrel. This radius reduces to a 0.5 inch over a 1-3/4" bend length when the specimen is bent through 180°. A diagram of the test fixture is shown in Figure 6.

The test was performed by placing the specimen in the end clamps, and bending the specimen over a decreasing radius while at the test temperature. Tests were conducted at room temperature and -100°F. The specimen was observed on both the tension and the compression sides at various bend radii during the test. Visual observations were made on the effects of bending on both coating and base metal.

5. Oxidation Resistance - Bend Tests.-- Tests were conducted to determine oxidation resistance of coated specimens after various amounts of coating elongation. These tests were performed by exposing 1" x 4" coated specimens at 2000°F after elongating the coating various controlled amounts.

The same bend fixture was used for this test as was used for the Transition Temperature Bend Tests as described above. However, the elongation of the coating on the tension side of the 1" x 4" specimen was calculated as a function of bend radius.

Each coated specimen was elongated in increments of 0.25% or 0.50% in the bend test fixture. After each coating elongation the specimen was removed from the fixture and exposed to 2000°F in slowly moving air for one hour. The specimen was allowed to cool to room temperature and carefully examined for oxidation or coating damage. If there was no indication of failure the specimen was elongated again and re-exposed at 2000°F. This procedure of elongation and temperature exposure was continued until the specimen either exhibited coating failure or the specimen had been bent through the full 180°F.

6. X-Ray Diffraction and Emission Studies.-- Studies of coating composition were conducted in conjunction with the Phase II evaluation of process variables. These studies were conducted on specimens coated with

the Si-Cr-Al and Si-Cr-B systems. The work was performed on a General Electric XRD-5 Diffractometer using a Cobalt tube set at 6 millamps and 50 KVP. A Fe_2O_3 filter was used at the detector.

For x-ray diffraction studies coated specimens were placed in metallographic mounts with the coated surface parallel to the face of the mount. Specimens of 1" x 1/2" were used because of the large interception area of the x-ray beam. The mounted specimens were placed in the diffraction holder and a diffraction pattern was obtained at an x-ray take-off angle of 2° and a time constant of 4.0 seconds. The recorder scale was set for 500, 1000, or 2000 counts per second full-scale linear presentation as required. Angular measurements, 20, were made from 6° through 147°.

After the surface diffraction pattern was obtained, specimens were removed from the diffraction holder and approximately 1/2 mil of coating thickness was removed by polishing the surface. The specimen was then replaced in the holder and another diffraction pattern was obtained using the above procedure. Diffraction patterns were obtained at approximately 1/2 mil increments until only the base metal diffraction pattern was observed. Photomicrographs were made of the surface after removal of each 1/2 mil coating increment.

The diffraction patterns were analyzed using the ASTM-X-Ray Powder Data File (1960) to identify the compounds observed at various levels within the coating.

The x-ray emission studies were conducted on coated specimens of about 1/2" x 3/4". The specimens were mounted in metallographic mounts with one end approximately 10 mils higher than the other. The specimen was lightly polished in such a manner as to lap away the coating at an angle to the specimen surface. One end was lapped down to the base metal while the opposite end was not lapped at all. This procedure exposed each layer of coating to the surface.

The Spectrometer was fitted with a Heinrich Miniature Probe, manufactured by General Electric Company. The goniometer was adjusted to the peak intensity of the element in question using a 1 mm probe. The 1 mm probe was then replaced with a 100 micron probe to gain a higher signal intensity. Using this probe, the number of counts, at 0.25 mm intervals along the surface, was obtained for 100 second periods. The number of counts obtained by this method is related to the concentration of the element in question. Chromium and columbium distribution in the coating was determined in this manner.

7. Metallographic Examination.-- Metallographic examination, including photomicrographs, were made on coated and uncoated specimens to determine the effect of the coatings and the coating process on the base material. The nature and thickness of the various interfaces, diffusion zones, and layers within the coating were investigated during these examinations.

RESULTS

A. PHASE I

1. Examination of Uncoated Columbium Alloys.--Metallographic examination and tensile strength tests were conducted on the three columbium alloys in the "as received" condition. The certified analysis of the Cb-1 Zr, D-31, and C-103 alloys are shown in Table 1.

Photomicrographs of these alloys are shown in Figures 7, 8, and 9. As indicated in the figures, specimens were taken from opposite corners of each sheet of alloy and a third specimen was taken from the geometric center. It may be observed that the Cb-1 Zr was received in a partially recrystallized condition, while the D-31 and C-103 were received in the fully hard cold rolled condition.

During this examination a few metal defects were noted for the C-103 alloy. An example of a typical inclusion in the alloy is shown in Figure 10. However, the effect of such inclusions on oxidation resistance of coated C-103 was not determined because of the difficulty of detection. The D-31 and Cb-1 Zr did not appear to have similar inclusions or metal defects.

Tensile tests of the three alloys were conducted on uncoated specimens of the design shown in Figure 1. The 5" dimension of these specimens was transverse to the direction of rolling. Room temperature tensile properties are shown in Table 3. These results tended to verify the finding in the metallographic examination that the Cb-1 Zr was in a partially recrystallized condition, while the D-31 and C-103 were in the cold rolled condition.

2. Oxidation Resistance Tests.--Oxidation resistance tests, as part of Phase I, were performed to determine the two best coatings for use in evaluation of the effects of process variables. The tests were conducted by exposing coated specimens at 2300°F and 2600°F in moving air.

In order that a number of different coating systems could be evaluated quickly the initial tests were conducted on Cb-1 Zr. Sixty 1" x 1" x 0.020" Cb-1 Zr oxidation resistance specimens were prepared for testing. These tests were conducted to determine pack compositions which would deposit coatings with a melting or fusing temperature above the 2600°F test temperature. The results of these tests are shown in Table 4.

On the basis of these results, two of the coating systems were chosen for further evaluation. One of the systems consisted of a coating deposited from a pack containing 60% silicon followed by a second coating deposited from a pack containing 35% chromium and 20% Al. This coating combination is designated as the Si-Cr-Al system

hereafter in this report. The other system consisted of a coating deposited from a pack containing 60% silicon followed by a second coating deposited from a pack containing 30% chromium and 30% ferro-boron. This coating combination is designated as the Si-Cr-B system hereafter in this report.

The oxidation resistance of the two coating systems on C-103 and D-31 alloys was also determined. The results of these tests are shown in Table 5. It may be observed that the oxidation resistance of the coatings on all three alloys are comparable, ranging from three to five and one-half hours at 2600°F.

3. Tensile Strength of Coated Specimens.--Tensile tests of the three alloys were conducted on coated specimens of the design shown in Figure 1. These results are shown in Table 6.

Specimens of Cb-1 Zr coated with both systems were tested at room temperature to determine their effect on the alloy. Since this material was received in a partially recrystallized condition any changes in strength and elongation could be ascribed to the coating or coating process.

The average ultimate tensile strength of the Cb-1 Zr coated with the Si-Cr-Al system is shown in Table 6 to be 49,200 psi. Although they are not shown in the table the average 0.2% yield strength and elongation was found to be 29,800 psi and 20%, respectively, with this coating system. The average ultimate tensile of Cb-1 Zr coated with the Si-Cr-B was found to be 49,500 psi with an average 0.2% yield strength of 28,750 psi and elongation of 20%. By comparing strength values shown in Tables 3 and 6 for coated and uncoated Cb-1 Zr it may be seen that the coating and coating process had a negligible effect on the strength properties of this alloy.

Elevated temperatures test up to 2500°F were conducted on coated specimens to determine a satisfactory static load for the succeeding Load Cycle Tests. The tensile properties at elevated temperature were determined by heating the coated specimens to temperature in air with quartz lamps, stabilizing for five minutes, and pulling the specimens at a load rate of 0.005" per minute until failure. Only a limited number of specimens were tested for tensile strength at elevated temperature, thus the strength values should not be considered exact. However, the results are generally in agreement with reported strengths of the uncoated alloys as shown in Table 4. No elongation values are shown because of rapid oxidation, and consequent loss of specimen length, as soon as ultimate failure occurred. However, it was evident during these tests, and during succeeding static load tests, that the specimen elongation was much greater than 10% before oxidation began. The results of these tests are also shown in Table 6.

4. Load Cycle Tests.--A knowledge of the effect of sustained

loads on coated columbium alloys during thermal cycling was desired as an indication of the high temperature oxidation protection characteristics of the coating. Difficulty was encountered in establishing the static load to be maintained during the load cycle tests. As described in Test Procedure, the specimens were held at a constant load during thermal cycling. Initially, a value of 60% of ultimate strength was chosen as the static load. When this stress level was used with coated D-31 the specimens tended to creep excessively, making satisfactory data unobtainable. For instance, a D-31 specimen was placed under a sustained load of 6500 psi (60% of 10,800 psi) for seven minutes at 2500°F. The specimen elongated 38% over a 2" length.

It was then necessary to establish a load which would not produce excessive creep at 2500°F. To determine this stress level a group of coated specimens were loaded at increasing load levels starting at 1000 psi and held at 2500°F for seven minutes. These results, Table 7, show loads in excess of 2000 psi give appreciable elongation at 2500°F. On the basis of these tests it was decided a load no greater than 2000 psi would be used for the Load Cycle Tests.

The Load Cycle Tests were performed at static loads of 1000 and 2000 psi. Visual examination of these specimens indicated loading was a factor in the failures. Table 8 shows Cb-1 Zr specimens tested at 2500°F under a load of 2000 psi withstood only 3 cycles for one specimen and 2 cycles for another specimen. The same alloy tested with a 1000 psi withstood an average of 5 cycles for four specimens. Although no elongation measurements of failed specimens could be made, it was apparent from the neck-down portion of the tensile specimens that significant elongation had taken place. The literature reports that the Cb-1% Zr alloy has an ultimate strength of 13,000 psi at 2000°F. An extrapolation of this value to 2500°F indicates a strength level for Cb-1 Zr of only a few hundred pounds per square inch. Thus, it would be expected this alloy would not be able to withstand more than a few cycles under any loading.

The number of cycles withstood by D-31 and C-103 specimens also indicate loading had a decided effect on durability under thermal shock. The coated C-103 specimens withstood an average of 5 cycles under a load of 2000 psi, and an average of 13 cycles under a load of 1000 psi. The D-31 specimen showed the same trend with an average of 7 cycles under a 2000 psi load, and 15 cycles under a 1000 psi load. No major differences were evidenced by the load cycle test results which would indicate an advantage of one of the coatings over the other.

These tests were conducted on coatings which have since been improved as a result of data obtained from the Phase II work.

5. Transition Temperature Bend Tests.--Bend tests, as described

in Test Procedure, were performed on coated and uncoated specimens of all three alloys. These tests were conducted at room temperature and -100°F .

The uncoated alloy was bent at both temperatures through 180° on a one-half inch radius with no failure.

Cb-1 Zr specimens coated with the Si-Cr-B system and tested at room temperature had very small flakes of coating pop off on the compression side when the specimen was bent to a radius of $1-1/3"$. When the radius was reduced to $0.8"$ the coating popped off along a straight line across the one-inch width of the specimens. Further bending tended to produce an uneven radius and the specimen bent at a sharp angle where the metal was bare. There was no visible effect on the tension side of the bent specimen.

Three Cb-1 Zr specimens coated with the Si-Cr-B system were tested at -100°F . One specimen failed by breaking at a bend radius of 0.8-inch. The other two specimens failed by breaking at a bend radius of one-inch. There was no visible change in the coating prior to failure.

Three Cb-1 Zr specimens coated with the Si-Cr-Al system were tested at room temperature. The coating on one of the specimens flaked off along a straight line at a bend radius of $0.57"$, while the coating on the second specimen formed a line at a radius of $0.5"$. The third specimen did not develop a bare line across the specimen even when bent to a radius of $0.5"$, although there was a slight flaking off of coating when the radius was $0.57"$.

Three Cb-1 Zr specimens coated with the Si-Cr-Al system were tested at -100°F . Two of the specimens broke when bent to a radius of one-inch and the third specimen broke when bent to a radius of $1.1"$. There was no visible effect on the coating prior to failure.

Room temperature bend test results on coated D-31 and C-103 agreed closely with the results found for the coated Cb-1 Zr specimens. Coating specimens of D-31 and Cb-1 Zr tested at room temperature showed flaking of coating when the specimens were bent to a radius between $0.5"$ and $1.0"$ over the $1-1/2"$ free length. The coatings invariably had an initial flaking of coating along one edge and an almost immediate flaking off of the coating in a straight line across the one-inch width of the specimen. The coated C-103 specimens did not fail when bent to a $0.5"$ radius at room temperature.

Coated specimens of Cb-1 Zr and D-31 bent at -100°F broke cleanly into two pieces with no prior effect on the coating. The C-103 coated specimens did not break, but exhibited a flaking off of the coating similar to that exhibited by the room temperature specimens.

Results of these tests are given in Table 9.

6. Metallographic Inspection.--The effect of the unoptimized coating process for deposition of the Si-Cr-Al and Si-Cr-B systems on the base alloy was investigated by metallographic inspection of coatings on all three alloys.

A photomicrograph of Cb-1 Zr coated with the Si-Cr-Al system is shown in Figure 11. The coating thickness was found to be 0.0025", with a diffusion zone approximately 0.0001" thick at the coating-base material interface. Comparison of this figure with Figure 7 showed there was no significant change in recrystallization in the Cb-1 Zr caused by the coating process.

A photomicrograph of Cb-1 Zr coated with the Si-Cr-B system is shown in Figure 12. The coating thickness was found to be 0.002", with a diffusion zone approximately 0.00015" thick at the coating-base metal interface. As with the Si-Cr-Al system, comparison of this figure with Figure 7 showed there was no significant recrystallization in the Cb-1 Zr caused by the coating process.

Similar photomicrographs for the Si-Cr-Al system deposited on D-31 and C-103 are shown in Figures 13 and 14, respectively. The coating on both alloys was found to be between 0.0020" and 0.0025" thick. The D-31 had a 0.0002" thick diffusion zone at the coating-base metal interface, while the diffusion zone at the interface on the C-103 was found to be 0.0001" thick.

Comparison of photomicrographs shown in Figures 8 and 13 showed the D-31 was received in the cold worked condition and the coating process had induced a slight recrystallization. A similar comparison of Figures 9 and 14 showed the C-103 was also received in the cold worked condition and the coating process had induced no apparent recrystallization. These observations were also supported by the tensile tests on coated and uncoated specimens which were reported earlier.

B. PHASE II

At the beginning of the Phase II evaluation of process variables, it was desirable to gain an insight into the characteristics of the silicide coating without the masking effect of the Cr-Al or Cr-B second coatings. A series of specimens were prepared by depositing the silicide coating on Cb-1 Zr oxidation specimens at four different temperatures, 1700°F, 1900°F, 2100°F, and 2300°F. Metallographic examination was made to determine coating thickness and appearance. The effect of deposition temperature on thickness of the silicide coating is shown in Figure 15. The coating thickness varied over a range from less than 1 mil to approximately 6 mils by varying the deposition temperature. It may be noted there was no distinct diffusion zone between the coating and base metal although there was a dark zone at the interface.

Oxidation resistance tests on specimens with the silicide coating only showed all had melting points between 2400°F and 2500°F. The coatings became molten and glassy at these temperatures which apparently allowed rapid oxygen diffusion through the coating. This was borne out by inspection of specimens after testing. Inspection revealed the glassy coating contained a white material believed to be columbium oxide. These specimens failed by oxidation and destruction of the specimen in one to two hours at 2400°F. Earlier work showed that one of the major effects of the Cr-Al or Cr-B second coat was to raise the melting point of the coating and consequently increase the oxidation resistance at 2600°F.

1. Effect of Retort Seal Variations.-- The first significant variable evaluated was the effect of retort seal characteristics. These variations were performed by using seal materials of widely varying permeability. The two retort seal materials consisted of the following: (a) Ottawa Flint Shot silica sand from Ottawa Sand Company, and (b) Ottawa Flint Shot sand and used pack material mixture, at a ratio of 70 to 30 parts by weight.

The efficiency of the retort seal was highly dependent upon the permeability of the seal materials. The method used for measuring permeability was developed by the American Foundrymen's Society. By this method the Permeability Number is defined as the rate in cubic centimeters per minute of air which will pass through a sand volume one square centimeter in cross section and one centimeter high under a pressure of 10 grams per square centimeter, Ref. 3. The permeability of the seal materials used in this evaluation was approximately 400 cubic centimeters of air per minute for the silica sand and 40 to 60 cubic centimeters of air per minute for the sand-used pack material mixture. These seal materials are denoted as high permeability for the sand, and as low permeability for the sand-used pack material mixture.

In order to obtain a better understanding of the coating process each variable was evaluated in conjunction with a second variable which was considered to be inter-dependent. This procedure allowed a statistical analysis of the effect of each variable as well as their interactions. In this group of retort seal tests the effect of varying the deposition temperature for each coating was determined for each type of retort seal.

The extent of this evaluation on the Si-Cr-Al system is shown in Table X. These results show the most oxidation resistant coatings were obtained by using a low permeability retort seal for the silicide first coating, and a high permeability retort seal for the Cr-Al second coating. Oxidation resistance of 5 to 8 hours was obtained when this retort seal combination was used. It may be noted that using a low permeability seal on the Cr-Al coating resulted in a final coating with a melting point of approximately 2500°F. These melting point variations indicated a large difference in the efficiency of the Cr-Al deposition reaction with retort seals of different permeability.

Coatings prepared with a high permeability seal for the initial silicide coating had poor oxidation resistance. This was to be expected as a result of surface oxidation of the columbium metal in the retort before the silicide deposition reaction was initiated. This surface oxidation inhibited proper formation of the silicide and subsequent poor oxidation resistance characteristics.

The same retort seal combination which yielded the best results with the Si-Cr-Al system also yielded the best results with the Si-Cr-B system. Table 11 shows that maximum oxidation resistance was obtained with a low permeability seal for the silicide first coat and a high permeability seal for the Cr-B second coat.

It was noted, as with the Si-Cr-Al system, that a low permeability seal with Cr-B second coating resulted in a final coat with a melting point of approximately 2500°F. This low melting point indicated a large difference in the efficiency of the second coat deposition reaction for both coating systems resulting from seal permeability differences. This difference is illustrated by a series of photomicrographs taken during the evaluation. In Figure 16, Photomicrograph (a) shows a silicide coating without a subsequent second coating. A definite columnar structure is observed in the silicide formation with no observable diffusion layer in the coating. Photomicrograph (b) shows a specimen coated with Si-Cr-B which had a low permeability retort seal used with the Cr-B coating. It may be observed that there is still a columnar structure in the major portion of the coating thickness. The grain structure of the coating appears to have been enlarged by the treatment required to deposit the Cr-B coating. The Cr-B was deposited at 2300°F for 16 hours. In addition, a diffusion zone may be observed at the coating-base metal interface. Later oxidation tests at 2600°F showed that specimens in this group melted at approximately 2500°F. Photomicrograph (c) shows a specimen coated with Si-Cr-B which had a high permeability retort seal used with the Cr-B coating. It is observed that a diffusion zone is now present at approximately the middle of the coating. The columnar structure has been completely obliterated above this diffusion zone and the crystal size has been decreased below this zone. Again it may be observed that a diffusion zone has been formed at the coating-base metal interface. This set of specimens were found to withstand 2600°F for 5 hours in subsequent testing. Results of the oxidation resistance test are shown in Table 11.

A more thorough discussion of the structure and composition of the coating is given with the x-ray emission and diffraction studies in the following sections of this report.

2. Effect of Coating Deposition Time and Temperature.--- The best retort seal combination as determined above was incorporated in the evaluation of coating deposition time and temperature variations. The extent of the evaluation on the Si-Cr-Al system is shown in Tables 12, 13, 14, and 15. Silicide coatings were first deposited on Cb-1 Zr oxidation test specimens at 1700°F, 1900°F, 2100°F, and 2300°F. The Cr-Al second coat was then deposited on these specimens as shown in the tables.

Data in Table 12 indicates that a coating consisting of a silicide first coat deposited at 1700°F (approximately 0.0008" thick) does not provide enough overall coating thickness to withstand 2600°F exposure regardless of what time or temperature is used in depositing the Cr-Al coating. It may also be observed that the coating thicknesses shown are indicative of the silicide first coat and the overall coating thickness is only slightly increased by the Cr-Al second coat. Replication specimens were not run on these variations since it was obvious the oxidation resistance of any of the replication specimens with the Si first coat deposited at 1700°F would be poor. Photomicrographs of coatings applied in this set of specimens is shown in Figure 17.

Results shown in Table 13 indicate oxidation resistance from 2 to 7 hours when the Cr-Al second coat was deposited at temperatures between 1900°F and 2300°F over a silicide coating deposited at 1900°F. Again it may be observed that the Cr-Al second coat did not appreciably increase the overall thickness of the coating. Photomicrographs typical of this group are shown in Figure 18.

Oxidation resistance of specimens reported in Table 14 was the best found in this portion of the evaluation. Two sets of specimens, silicide coating deposited at 2100°F with Cr-Al coating deposited at 2300°F, withstood 10 hours at 2600°F. Typical coatings of this group are shown in Figure 19.

Tests on these specimens were stopped at 10 hours so specimens could be mounted and examined metallurgically. Figure 20 shows the appearance of one of the Si-Cr-Al specimens which had withstood 10 hours at 2600°F. Comparison of this figure with the lower photomicrograph of Figure 19 shows negligible oxygen penetration into the coating. The diffusion zone nearest the base metal has broadened slightly, and an oxide layer has been formed on the outer surface. This outer oxide formation had a dark green appearance similar to that of chromium oxide.

Results of Table 15 show specimens with a silicide coating deposited at 2300°F did not give oxidation resistance at edges of specimens at exposures as low as 2400°F and 2500°F. It was noted the silicide coatings had a tendency to form cracks and fissures at the sharp radii. It was apparent the silicide coatings formed at 2300°F are too thick to allow contraction of the coating during cooling without shrinkage cracks around the 0.010" radius. A thicker material, with more generous radii at edges and corners would probably be free of the difficulties with these 0.006" to 0.008" coating thicknesses. Typical coatings produced in this group are shown in Figure 21.

The Si-Cr-B system was evaluated in the same manner as the Si-Cr-Al system. The silicide coating was first deposited on Cb-1 Zr alloy oxidation test specimens at 1900°F and 2100°F. The Cr-B second was then deposited on these specimens at the desired temperature. No specimens with the silicide first coat deposited at 1700°F and 2300°F were produced since it was apparent from results of tests on the Si-Cr-Al system that these temperatures would not produce satisfactory coatings.

Table 16 shows the effect of the Cr-B second coat deposition time and temperature on coating thickness and oxidation resistance when deposited over a silicide coat formed at 1900°F for 16 hours. It may be observed that Cr-B deposition at 1700°F resulted in a coating which melted at approximately 2600°F. The most oxidation resistant coatings formed in this group were those which had the Cr-B deposited at 2100°F.

An illustration of the effect of varying times and temperatures on the second coating for the Si-Cr-B system is shown in Figure 22. This figure shows photomicrographs of some of the coatings reported in Table 16. The silicide first coat was approximately 0.002" thick on all the specimens shown in the figure. The effect of the Cr-B second coat on the silicide deposit may be observed by comparison of these photomicrographs. In Photomicrograph (a) Cr-B deposited at 1900°F for 16 hours appears to have changed the basic silicide coating only slightly. The columnar structure characteristic of the silicide is no longer apparent, however, and a thin layer of chromium-boron rich coating has formed on the surface. There are no definite diffusion boundaries in the coating except at the interface of the silicide coating and the chromium-boron coating. This coating was found to withstand oxidation at 2600°F for 2 hours. In Photomicrograph (b) the Cr-B treatment at 2100°F for 16 hours has caused a considerable change in the silicide coating. The chromium-boron rich layer now extends to approximately 1/3 the depth of the coating. There is also a diffusion zone interface at the approximate center of the coating and another diffusion zone at the coating-base metal interface. Oxidation tests showed this coating capable of withstanding 3 hours at 2600°F.

Photomicrograph (c) shows the results of Cr-B deposited at 2300°F for 10 hours. The Cr-B rich layer still covers only approximately 1/3 of the total thickness. However, the diffusion zone which was barely apparent in Photomicrograph (b) has proceeded approximately 8/10 of the way through the coating. It may be observed that the structure of this zone is composed of relatively large crystals with no apparent orientation. The x-ray diffraction studies discussed in a later section indicated this zone to be boron rich with only a small percentage of chromium present. There is also another diffusion zone at the coating-base metal interface. Specimens processed in this group withstood oxidation for 3 hours at 2600°F. Photomicrograph (d) shows the results Cr-B deposited at 2300°F for 22 hours. It is apparent that diffusion during the Cr-B deposition had proceeded throughout the silicide coat and completely changed the coating structure. These specimens failed by oxidation at the edges during the first hour exposure at 2600°F. However, it should be noted that the coating on the flat portions of these specimens appeared to have excellent oxidation resistance even though they had edge failure after a short period of exposure.

Photomicrographs of the specimens reported in Table 17 with the silicide deposited at 2100°F revealed the same Cr-B time-temperature diffusion characteristics discussed above.

Observation of the specimens reported in Tables 16 and 17 for the Cr-B second coat and in the previous tables for the Cr-Al second coat led to the observation that second coat deposition temperatures in the range from 2100°F to 2300°F for both systems produced finished coatings which would withstand 2600°F. On the basis of these results, it was decided that the intermediate temperature of 2200°F would be used in depositing both types of second coats. An examination of this data did not reveal a marked increase in oxidation resistance for specimens run at different times at the same temperature. In view of these observations it was decided that Cr-Al and Cr-B coating deposition would be run for 16 hours.

A representation of the various steps of preparation and testing involved in these oxidation tests is shown in Figure 23. At the upper left hand corner of the figure is shown the results of a very short exposure of an uncoated Cb-1 Zr specimen in the oxidation test furnace. The thick white columbium oxide flakes which form almost immediately are shown around the exposed specimen. The "L" shaped specimens shown in the figure were oxidation resistance specimens which were cut for metallographic inspection.

A study was also conducted to determine the effect of variation of time and temperature on the silicide first coat. The first coat was deposited at 1900°F, 2100°F, and 2300°F for various times. The second coat, both Cr-Al and Cr-B, was run at 2200°F for 16 hours. This evaluation is shown in Tables 18 and 19.

The results in Table 18 show the effects of variation of silicide deposition time and temperature on the finished coating oxidation resistance. It was found that silicide deposition at 2100°F for 16 and 22 hours and at 2300°F for 10 hours resulted in coatings capable of withstanding 2600°F for 10 hours. No runs were made to deposit the silicide for periods longer than 10 hours at 2300°F since it has been shown that longer times result in formation of excessive silicide thicknesses. An example of the Si-Cr-Al coatings produced in these tests before and after exposure for 10 hours is shown in Figure 24.

Similar results for silicide deposition time and temperature were found for the Si-Cr-B system. Table 19 shows the results of this evaluation. It was again found that silicide deposition at 2100°F for 16 and 22 hours and at 2300°F for 10 hours results in coatings capable of withstanding 10 hours at 2600°F. An example of the Si-Cr-B coating system before and after exposure for 10 hours is shown in Figure 25.

On the basis of this evaluation, it was decided that subsequent runs for the silicide first coat would be made at 2100°F for 16 hours.

3. Effect of Pack Mix Particle Size and Pack Density Variation.-- The intention at the start of the program was to eliminate one of the two candidate coating systems during the time-temperature study. Then the evaluation of particle size and pack density variations would be conducted on only one coating. However, as shown in the earlier evaluations, both the Si-Cr-Al system and the Si-Cr-B system appeared to perform approximately the same in oxidation resistance tests. In order to complete all the desired tests, it was necessary to proceed with only one coating system for the remainder of the Phase II. It was decided that only the Si-Cr-Al system would be used.

Since the two systems exhibited similar oxidation resistance characteristics, it appeared any improvement found for the Si-Cr-Al system would be an improvement for the Si-Cr-B system. At the end of the Phase II evaluation, the process conditions chosen as best for Si-Cr-Al would be used in producing replicated specimens of both coating systems and these results would determine which system to use in preparing test components in Phase III.

The evaluation of the effect of variation of pack mix particle size was conducted by varying particle size of the inert material, alumina, in the pack. It was believed that an increase in coating durability could be obtained by using an alumina powder sufficiently large to allow a free flow of gas within the retort during the coating process. The particle size variation was obtained by using two types of alumina powder of widely differing mesh size.

The fine mesh size alumina was 325 mesh tabular alumina, Grade T-61, manufactured by the Aluminum Company of America. The coarse mesh alumina was sieved from E-163 alumina bubbles, manufactured by The Norton Co., Worcester, Massachusetts. These alumina particles ranged in size from 10 to 20 mesh. This size range was chosen because it appeared to offer enough size variation in the pack to allow free gas flow.

Specimens were prepared with 325 mesh and 10 - 20 mesh alumina in the silicide first coat pack. These specimens were then coated with the Cr-Al coating, also with and without the large particle size alumina.

The effect of particle size variations were evaluated in conjunction with pack density variation. Pack density variation was accomplished by vibrating some of the pack mixtures used in the particle size evaluation. Pack density variations were accomplished by placing loaded retorts on a Syntron Vibratory Parts Feeder, Type LP01B, which was equipped with a 12" flat platform. Vibration intensity was controlled by a Syntron Electric Controller, Type LOC01, with an arbitrary scale from 0 to 100. A scale setting of 20 was used in vibrating the retorts for this evaluation.

It was expected that the combination of particle size variations and pack settling by vibration would cause a fairly wide variation in pack density. However, the density range was not as large as was desired. The density could not have been varied over a wider range without changing the pack composition which would have introduced other variables into the evaluation. The density of the silicide pack mix, 60% silicon metal powder -

30 alumina - 10% halide, varied from 0.0299 pound per cubic inch to 0.0336 pounds per cubic inch, a 12.6% variation in density. The density of the Cr-Al pack mix, 30% chromium metal powder - 30% aluminum metal powder - 33% alumina - 7% halide, varied from 0.0322 pounds per cubic inch to 0.0344 pounds per cubic inch, a 6.8% density variation.

This evaluation and results of oxidation tests are shown in Table 20. The maximum oxidation resistance in this group of specimens was obtained with the fine particle size alumina in both the silicide first coat and the Cr-Al second coat. Changes in pack density afforded by vibrating the packed retorts did not appear to materially affect oxidation resistance of coated specimens. The large particle alumina appeared to allow the silicide first coat average thickness to build up slightly more than the coatings produced with the 325 mesh alumina. However, the differences appeared to be small, approximately $\frac{1}{2}$ mil difference. The specimens produced with the 10 - 20 mesh alumina tended to fail on the specimen face after short 2600°F exposure. This appeared to be caused by formation of a thin silicide coat where the alumina particles touched the base metal.

4. Effect of Pack Composition Variations.-- The variation in pack composition which is most pertinent to oxidation resistance is the content of halide in the pack mix. Halide content of 10% in the silicide pack mix had been used in all preceding evaluations, as well as a content of 7% in the Cr-Al pack mix. In this evaluation, the halide composition in the silicide coat was 6, 10, and 14% and 4, 7 and 10% in the Cr-Al coat.

The results of these tests are shown in Table 21. It may be observed that the best results were obtained at halide contents of 6 and 10% in the silicide first coat and 4% for the Cr-Al second coat. It may also be observed that a 14% halide content in the silicide pack mix decreases the oxidation resistance. Also, a halide content of 7 and 10% in the Cr-Al second coat had decreased durability.

C. STATISTICAL ANALYSIS

In order to determine the independent effect of each variable investigated the results of the Phase II tests shown in Tables 11 through 20 were analyzed by statistical methods. This analysis included a factorial analysis, where possible, of the top six performance groups for each variable and a series of "t" tests to determine significant differences.

For example, the analysis as applied to the coating process temperature was first developed into a 2×3 factorial analysis of the six best performance groups of specimens coated at different temperatures. The total hours of exposure at 2600°F of specimens processed at different temperatures were tabulated and analyzed by a sum of the squares analysis.

The oxidation resistance test data was analyzed for the effect of furnace time "t" test by taking as the Cr-Al furnace process time in hours. The oxidation resistance data for the top six performance cases was as follows:

CORRECTED DATA				
T (time in Hours)	10	16	22	
T_{Si} 1900°F)	2	2	3	
T_{CrAl} 1900°F)	1	4	2	
T_{Si} 1900°F)	3	3	4	
T_{CrAl} 2100°F)	2	3	3	
T_{Si} 1900°F)	4	7	6	
T_{CrAl} 2300°F)	4	5	6	
T_{Si} 2100°F)	1	4	4	
T_{CrAl} 1900°F)	3	6	6	
T_{Si} 2100°F)	5	6	7	
T_{CrAl} 2100°F)	6	7	6	
T_{Si} 2100°F)	8	9	10*	
T_{CrAl} 2300°F)	8	10	10*	

* Test stopped

Values shown are one hour less than number of hours when oxidation was observed

The "F" test factorial analysis of the six best performance groups processed at three different times for each temperature are shown below.

Cr-Al Coating Furnace Temperature	1900°F	2100°F	Totals
1900°F	14	24	38
2100°F	18	37	55
2300°F	32	54	86
Totals	64	115	179

$$\text{Correction Factor} = \frac{(179)^2}{36} = 890.03$$

Total Sum of Squares = $\sum_{i=1}^{36} (X_i)^2 - CF$ where the X_i are the 36 values shown in table of corrected data above.

$$\begin{aligned} \text{Total Sum of Squares} &= 1126 - 890.0 \\ &= 236 \end{aligned}$$

$$T_{Si} \text{ Sum of Squares} = \frac{(64)^2 + (115)^2}{(36 \div 2)} - CF = 72.25$$

$$T_{CrAl} \text{ Sum of Squares} = \frac{(38)^2 + (55)^2 + (86)^2}{(36 \div 3)} - CF = 98.72$$

$$\text{Treatment S of S's} = \frac{(14)^2 + \dots + (54)^2}{(36 \div 6)} - CF = 177.5$$

$$\text{Interaction } (T_{Si} \times T_{CrAl}) \text{ S.S.} = 177.5 - 72.3 - 98.7 = 6.50$$

An analysis of the variances from the preceding revealed the following information:

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	"F"
Total	35	236.0		
Treatment	5	177.5	35.5	18.21**
T_{Si}	1	72.25	72.25	37.05**
T_{CrAl}	2	98.72	49.36	25.31**
Interaction	2	6.5	3.25	1.67

** Since tabular "F" for 5 and 30 degrees of freedom is 3.70 at the 99% confidence level, treatments are highly significant. Tabular "F" (99% level) for 1 and 3 d.f. is 7.56, and for 2 and 30 d.f. is 5.39. Hence, there is a highly significant difference in oxidation due to both Si treatment and Cr-Al treatment process furnace temperature.

/ Not significant at 95% level, for tabular "F" for 2 and 30 degrees of freedom is 3.32. Had interaction been significant, the interaction mean square would have been used instead of the error mean squares, to obtain the other "F" values.

The following are the "t" test calculations for Si coating at 2100°F and Cr-Al coating at 2300°F.

t (Time Hours)	10	16	22
Specimen 1 (hours)	8	9	10
Specimen 2 (hours)	8	10	10
Totals	16	19	20

The estimate of the population variance in the "t = 10 hours" case is:

$$s_x^2 = \frac{(8^2 + 8^2) - \frac{(8 + 8)^2}{1}}{1} = 128 - 128 = 0$$

The estimate of the population variance in the "t = 16 hours" case is:

$$s_y^2 = \frac{(9^2 + 10^2) - \frac{(9 + 10)^2}{1}}{1} = 181 - \frac{361}{2} = 0.5$$

$$s^2 = \frac{0 + 0.5}{1 + 1} = 0.25, \text{ whence}$$

$$s = 0.5$$

Now $t = \frac{\bar{y} - \bar{x}}{s}$ if the mean of 10 hour reading is equal to the mean of the 16 hour reading, which is hypothesized to be the case,

$$\text{where } s_{\bar{y} - \bar{x}} = s \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}$$

Our $n_1 = n_2 = 2$ and $s = 0.5$

$$\text{Thus, } s_{\bar{y} - \bar{x}} = 0.5 \sqrt{\frac{1}{2} + \frac{1}{2}} = 0.5 \sqrt{1} = 0.5$$

Since $\bar{y} - \bar{x} = 1.5 \text{ hours}$

$$t = \frac{1.5}{0.5} = 3.0$$

For a significant difference "t" value (calculated) with 2 degrees of freedom, for $(n_1 - 1) + (n_2 - 1) = 2$, must fall between -4.303 and $+4.303$ (from "t" table) in 95% of the cases. The calculated "t" value, 3.0, is within these limits so the t-test has failed to show a significant difference between the oxidation times using furnace times of 10 and 16 hours. From the data obtained, 16 hours does not surpass 10 hours in 95% of the cases which arise, when the Si coating is put on at 2100°F and the Cr-Al coating is put on at 2300°F .

A "t" test was developed to determine the statistical advantage of using 2300°F instead of 2100°F for the second coating processing temperature.

Using the last two groups of six values each from the foregoing table.

$2100^{\circ}\text{F}/2100^{\circ}\text{F}$

$$\begin{aligned} x_1 & \\ 5 & \\ 6 & \\ 6 & \\ 7 & \\ 7 & \\ 6 & \\ \Sigma x & = \frac{37}{6} \\ x & = 6.17 \end{aligned}$$

$2100^{\circ}\text{F}/2300^{\circ}\text{F}$

$$\begin{aligned} y_1 & \\ 8 & \\ 8 & \\ 9 & \\ 10 & \\ 10 & \\ 10 & \\ \Sigma y & = \frac{55}{6} \\ y & = 9.17, \bar{y} - \bar{x} = 3.0 \end{aligned}$$

So that

$$s_x^2 = \frac{\sum (x_i)^2 - \frac{(\Sigma x)^2}{n}}{n-1} = \frac{231 - \frac{(37)^2}{6}}{5} = 0.56,$$

$$s_y^2 = \frac{509 - \frac{(55)^2}{6}}{5} = 0.96$$

$$s^2 = \frac{0.56 + 0.96}{5+5} = \frac{1.52}{10} = 0.152$$

$$s = \sqrt{0.152} = .39$$

$$s_{\bar{y} - \bar{x}} = s \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} = .39 \sqrt{\frac{1}{6} + \frac{1}{6}}$$

$$s_{\bar{y} - \bar{x}} = .39 \sqrt{.3333} = .39 (.5773)$$

$$s_{\bar{y} - \bar{x}} = .225$$

$$t = \frac{3.0}{.225} = 13.3$$

Students "t" for 10 degrees of freedom at the 99% confidence level is 3.169. Hence, our calculated t is more than three times as large as required for 99% confidence that 2100°F/2300°F is better than 2100°F/2100°F.

On the basis of tests similar to those illustrated above, the effects of the process variables were analyzed to determine the optimum process conditions. It should be noted that the tests for particle sizes, pack density, and pack composition had insufficient numbers of test samples to conduct a complete analysis of the effect of those variables. On the basis of the results reported in Phase II, the most favorable coating process is obtained by procedures using the following conditions:

Coating Variable	Silicide Coating	Cr-Al Coating
Retort Seal	Low permeability	High permeability
Furnace Process Temp.	At least 2100°F	2300°F
Furnace Process Time	16-22 Hours	16-22 Hours
Particle Size	Fine (325 Mesh)	Fine (325 Mesh)
Particle Density	Low	Low
Pack Composition	6 to 10% Halide	4% Halide

The data supports a process for the Si-Cr-B system like the one defined above in which the silicide coating is applied at 2100°F for 16 to 22 hours and the Cr-B coating applied at 2200°F to 2300°F for 16 hours. A longer period of time for coating might be better, but the necessity of a longer period was not established.

D. ANALYTICAL EVALUATION

Near the end of the Phase II process evaluation, an analytical study was initiated by use of x-ray emission and diffraction techniques and metallographic examination. This study was made on specimens coated with silicide only, the Si-Cr-Al system, and the Si-Cr-B system.

It should be mentioned that the coating components containing columbium are reported by the chemically synonymous name of niobium (Nb). This is necessary since the ASTM x-ray Power Data File lists the metal and its compounds by this nomenclature.

1. Silicide Coating. -- Five Cb-1Zr specimens coated with silicide were examined by x-ray diffraction. These specimens were prepared as follows: (a) 1900°F for four hours; (b) 1900°F for eight hours; (c) 1900°F for 16 hours; (d) 1900° for 24 hours; and (e) 2100°F for 16 hours.

The specimen prepared at 1900°F for four hours was found to be incompletely coated, as shown by the presence of the characteristic niobium diffractions peaks in the diffraction pattern. Diffraction peaks were also observed for Nb_5Si_3 (tetragonal) and $NbSi_2$.

A representation of the coating prepared at 2100°F for 16 hours is shown in Figure 26. Diffraction patterns of the coating were obtained on sections taken parallel to the specimen surface at 1/2 mil increments. A representative cross section of the coating at approximately 1500X is shown at the top of Figure 26. Photomicrographs of the surfaces were taken at each increment of thickness through the coating. Portions of these photomicrographs are shown in the figure at their approximate location in relation to the cross section.

The chemical identification directly below the cross section denotes the composition found at that coating depth. The only component found in this specimen was $NbSi_2$, oriented with the 110 crystal plane parallel to the metal surface. An orientation of this nature would require that crystal growth be parallel to the 001 axis direction or perpendicular to the metal surface. The assumption of orientation in the 110 plane is based on the very strong reflections from the 110 and 220 planes and the reduced intensity of reflections from the 111 plane. A normal intensity distribution, corresponding to the ASTM data, had been observed on earlier specimens.

2. Si-Cr-Al System. -- A Cr-1 Zr specimen was coated with silicide at 2100°F for 16 hours and Cr-Al at 2200°F for 16 hours and prepared for x-ray emission and diffraction studies as described in the Test Procedure. These x-ray determinations were made at approximately 0.0005" increments of coating depth. A representation of coating cross section at 1500X, qualitative coating composition at various depths, and photomicrographs of the polished surface at various depths is shown in Figure 27.

Further emission analysis with miniature probes showed that the chromium content decreased rapidly as shown in Figure 27, and at a depth below about one-third of the thickness of the coating it constituted only a small portion of the coating components. The niobium was found to be present throughout the coating, but at a low concentration where the chromium was high. The concentrations of the elements varied as would be expected for a diffusion process of this nature. The figure thus gives a good indication of the extent of chromium diffusion during the 16-hour Cr-Al coating process.

Attempts to use a helium tunnel for determination of the lighter elements silicon and aluminum, with the 1 mm miniature probe were unsuccessful because of the long range of the weak X-rays produced.

X-ray diffraction studies tended to support the findings in the emission studies. The coating compounds found in this study are shown in Figure 27 at the approximate depths where each determination was made. Near the outer surface, NbAl_3 , Al_5Cr , and Alpha Al_2O_3 were found to be present. At slightly greater depths, the Nb Si_2 increased and Cr_3Si and NbCr_2 were indicated. Gradually, all chromium and aluminum compounds disappeared and only the oriented NbSi_2 was present. Nb_5Si_3 was observed in the Si-Cr-Al coating only near the base metal coating interface.

A group of curves showing the approximate change in coating composition with thickness are shown in Figure 27. These curves are based on results of information obtained from X-ray emission analysis and X-ray diffraction studies in conjunction with the metallographic studies. The percentage of niobium and chromium at various coating depths was determined by comparing the specific emission count rate of these components in the coating with count rates produced by metal specimens containing known percentages of each component. The percentage of silicon was determined by using the composition of the portion of the coating, near the base metal, composed of predominately NbSi_2 as a reference percentage of approximately 36 per cent silicon by weight. The composition of aluminum was determined by difference using chromium, niobium, and silicon as the only other components in the coating. It is realized that the compositions shown are only approximations; however, they were helpful as guides in determining the effects of relative amounts of the various components in the coating.

3. Si-Cr-B System.-- X-ray diffraction and emission studies were made similar to those on the Si-Cr-Al system. Emission determinations for boron content are unobtainable due to the extremely soft nature of the X-rays produced by this element. Analytical studies were conducted on the Si-Cr-B system on Cb-1 Zr, C-102 and D-31 alloys. The coating process variables were those specified as optimum in the statistical evaluation.

A representation of coating cross section, and approximate coating composition at various depths is shown in Figures 28 and 29 for the Si-Cr-B coating on Cb-1 Zr and C-103. A similar representation for the coating on D-31 alloy is shown in Figure 30; however, no attempt was made to determine coating composition because of the presence of Ti in the alloy. The percentages of either titanium or boron in the coating could not be determined by emission analysis, making the determination of approximate composition curves impossible.

E. PHASE III

Work in Phase III was divided into three parts as follows: (1) determination of process reliability and reproducibility using information and data from Phase II; (2) selection of techniques for coating complex multi-component assemblies; and (3) delivery of coated test specimens and a test assembly to ASD.

(1) Process Reliability and Reproducibility

In order to determine process reliability and reproducibility, three identical sets of test specimens were coated and tested using the best process techniques as determined in Phase II. These replication specimens were processed according to the optimum conditions determined in Phase II. The specimen were replicated and tested as indicated below:

Alloy	Coating System	Retort			Test Specimens in Each Run
		1st	2nd	3rd	
Cb-1 Zr	Si-Cr-Al	1	1	1	3 oxidation - 2600°F 2 bend elongation
Cb-1 Zr	Si-Cr-B	1	1	1	3 oxidation - 2600°F 2 bend elongation
C-103	Si-Cr-Al	1	1	1	3 oxidation - 2600°F 2 bend elongation
C-103	Si-Cr-B	1	1	1	3 oxidation - 2600°F 2 bend elongation
D-31	Si-Cr-Al	1	1	1	3 oxidation - 2600°F 2 bend elongation
D-31	Si-Cr-Al	1	1	1	3 oxidation - 2600°F 2 bend elongation

The results of oxidation tests on the two optimized coating systems deposited on the three alloys are shown in Table 22. Maximum time to failure and average life of each specimen group is shown in the table. The average durability of the Si-Cr-Al coating for all replicated runs tested at 2600°F was found to be 8.8 hours on Cb-1 Zr, 9 hours on C-103, and 10.9 hours on D-31. The average durability at 2600°F of the Si-Cr-B system was found to be 11.2 hours on Cb-1 Zr, 11.4 hours on C-103, and 11.5 hours on D-31.

Recent publications concerning coating for other refractory metals, tungsten and molybdenum, indicated that difficulty has been experienced with oxidation of silicide coatings at relatively low temperatures (1000°-1600°F). (References 32, 33.)

It was believed this difficulty might also be prevalent on silicide coatings for tantalum and columbium. This phenomenon has been termed the "di-silicide pest" and appears to be associated with an intercrystalline oxidation of the di-silicide.

In order to determine the effects of such low temperature oxidation a set of specimens were coated with both systems and tested in this temperature range. The results of these tests are shown in Table 23. As indicated on the Table, the test cycle consisted of successive one hour exposures at 2000, 2400, 1000, 1200, 1400, 1600, 1800, 2000 and 2400°F. These results indicated a definite advantage of the Si-Cr-B system over the Si-Cr-Al system. All but two of the specimens coated with the Si-Cr-B withstood the full low temperature cycle, while all the specimens coated with Si-Cr-Al exhibited edge and face failures at temperatures between 1400°F and 2000°F.

The Phase III replication tests also included bend specimens which were evaluated for resistance to oxidation after being elongated various amounts on the transition temperature bend jig. (Figure 6) The procedure for conducting these tests are given in the section under Test Procedure. The results of these tests are shown in Table 24.

These results showed that the optimized Si-Cr-Al system was capable of being elongated to about 1% on Cb-1Zr and C-103 without a significant decrease in oxidation resistance. Similar specimens of Cb-1Zr and C-103 coated with the Si-Cr-B system were capable of being elongated about 2% before oxidation was noted in subsequent tests.

The specimens of D-31 coated with the Si-Cr-Al system broke in two pieces in the bend fixture after elongations of .7% to 1.0%. The same alloy coated with the Si-Cr-B system also broke in two pieces after elongation of about 1.4%.

It should be noted that all the coated specimens were elongated well past the normal 0.2% yield design value before there were any evidences of oxidation noted in subsequent tests.

Evaluation of the results of these Phase III tests showed a slight advantage in oxidation resistance at 2600°F for the Si-Cr-B and a large advantage in low temperature characteristics. On the basis of these considerations it was decided that the remaining specimens and assemblies in Phase III could be coated with the Si-Cr-B system.

(2) Selection of Acceptable Coating Techniques for Fasteners

The selection of coating techniques for component parts and fasteners for complex assemblies was evaluated by preparation of representative specimens fabricated with bolts, rivets, skin sections, welds and structural stiffeners. Examples of these specimens are shown in Figures 2 and 31 through 34.

Photographs showing the sequence of assembly are shown in Figure 36. The assembly was coated in three steps in order to adhere to the riveting and fastening sequence found to be best in earlier Phase III tests. The component parts were completely welded, formed and all holes drilled for riveting and fastening. The coating procedure consisted of depositing an initial silicide coating on each of the component parts. The parts were then riveted together into the complete assembly. A second silicide coating was then deposited on the assembly to cover areas which had been chipped in handling and to cover the bare, upset portion of the rivets. The assembly was then coated with the final Cr-B coating. A photograph showing the completed coated assembly is shown in Figure 37.

In order to better show the applicability of the structure, it was decided to test it under glide re-entry conditions as simulated by propane torch and ram-jet tests. These tests were performed by the Vought Aircraft and Missiles Division, Structures and Systems Laboratories.

The Propane Torch Facility consists of a variable number (1 to 13) of 1" diameter propane torch heads mounted in a circular pattern. These torches are mounted on a movable dolly which may be brought toward a stationary mounted specimen. Test temperatures up to 5000°F over a 10" diameter may be obtained, depending on gaseous mixtures and emissivity of test specimen materials.

The Ram-Jet Heater Facility consists of a 10-inch ram-jet burner equipped with an 8-inch diameter Mach 1.5 exhaust nozzle and a movable model support sting for test specimens. The ram-jet burner is capable of providing an 8-inch diameter exhaust gas stream at temperatures between 1400° and 4000°F. The maximum exhaust gas pressure is approximately 55 psi, with an over-all sound pressure level near the nozzle of approximately 190 decibels.

An idealized combination of re-entry conditions for glide vehicle leading edge surfaces is shown in Figure 38. These conditions indicate that during re-entry, such surfaces would encounter an approximate maximum temperature of 2400°F and a maximum dynamic surface pressure of 800 psi with an accompanying sound level of 140 decibels.

These re-entry conditions in the combinations shown are unattainable in one test facility. The ram-jet facility has sound and pressure levels much too high if the specimens are brought to a temperature of 2400°F. Conversely, if sound and pressure are adjusted to the proper levels, the temperature is about 1600°F. Thus, a compromise was necessary to attain all of the re-entry conditions. For these reasons, it was necessary that the assembly be tested at the proper sound and dynamic surface pressure

Examples of welded FS-82 alloy and riveted D-31 alloy test specimens coated with the Si-Cr-B system are shown in Figure 31. This figure shows FS-82 alloy specimens prepared by lap weld and resistance spot weld methods. Weld specimens which were coated and tested for oxidation resistance at 2500°F included the following: three FS-82 lap weld specimens, three FS-82 butt weld specimens, and three FS-82 resistance spot weld specimens. Oxidation tests at 2500°F on the butt weld specimens showed no difference in oxidation resistance between the welded and unwelded areas of the specimens. Similar oxidation tests on the lap weld and spot weld specimens indicated oxidation around the faying surfaces which indicated incomplete coatings in these areas. Examples of the lap weld and spot weld specimens exhibiting areas of oxidation around the faying surfaces are shown in Figure 32. On the basis of these tests it was decided that any later welds in components and assemblies should be butt welds.

Typical examples of riveted lap shear specimens coated with the Si-Cr-B system are shown in Figure 33. A total of nine D-31 riveted specimens were prepared by three different coating procedures. The three different procedures were as follows: (1) drill rivet holes, coat rivets and specimen parts with silicide first coat, rivet, recoat with silicide coating and coat with Cr-B final coat; (2) coat rivets and specimen parts with silicide first coat, drill rivet holes, rivet, recoat with silicide coating and coat with Cr-B final coat; (3) drill rivet holes, rivet, coat with silicide first coat and coat with Cr-B final coat. These were tested for shear strength at 2200°F. The results of the lap shear tensile strength tests are shown in Table 25.

On the basis of the preceding tests on riveted lap shear specimens, it was decided that the method to be used in the riveted portion of the later leading edge structure would be as follows: drill all rivet holes prior to coating; make all necessary welds, coat all component parts with silicide first coat; make all rivet fastenings; coat with second silicide coat; coat with Cr-B second coat.

The work in the second portion of Phase III culminated in the fabrication and testing of a simulated leading edge assembly comprised entirely of columbium alloy components coated with the Si-Cr-B system. A drawing of the assembly is shown in Figure 34. All of the component parts were fabricated by the Research Manufacturing Group of the Astro-nautics Division of Chance Vought Corporation. Components were fabricated from bare sheet, rod, and bar stock. The assembly was fabricated as part of the company sponsored research and development work on refractory alloys. After fabrication and coating the assembly was evaluated in typical re-entry conditions.

The purpose for fabricating, coating and testing the assembly was to show the feasibility of employing different techniques of manufacture which had been shown to perform satisfactorily in earlier Phase III oxidation tests. Examples of the butt welds used in the assembly are shown

levels in the Ram-Jet Facility. The assembly was tested at the maximum desired temperature in the Propane Torch Facility.

The temperatures attained in the Propane Torch Test are shown in Figure 39. It may be observed that a maximum temperature of 2500°F was reached, which exceeded the maximum re-entry temperature of 2350°F as shown in Figure 38. The temperature was measured with an optical pyrometer and corrected with an assumed emissivity of 0.85. The total test time above 2000°F was 30 minutes with an idealized re-entry time of 25 minutes. A photograph showing the top surface and bottom side of the assembly after the ram-jet test is shown in Figures 40 and 41. The top surface shown was the surface exposed to the maximum temperature during the test. There was no evidence of oxidation on the surface or around the rivets after completion of this test. The appearance of the surface indicated the assembly would be able to withstand the re-entry temperature conditions for many more cycles.

The conditions attained in the Ram-Jet Facility are shown in Figure 42. It may be noted that the sound level exceeded the test requirement of 140 decibels by a level of 30 decibels. This represents a sound energy level of approximately 10 times the level necessary to withstand the re-entry conditions. It may also be observed that a dynamic pressure of 1200 psi was attained, which also exceeded the re-entry condition requirements of 800 psi.

There was no evidence of detrimental effects on the assembly during this test under the conditions of maximum sound level and surface pressure shown for the typical re-entry conditions in Figure 38. Structural failure due to the combined effects of sound and pressure on the 1" unsupported .020" thick trailing edge did occur at the maximum points shown in Figure 42. At these points, well above the required conditions of sound and surface pressure, portions of the trailing edge broke and separated from the assembly. Close inspection after the test revealed no evidence of oxidation or other detrimental effects on the coating except along the broken edges of the specimen. There was no sign of erosion damage to the coating even around rivets, welds, or sharp edges.

A photograph showing the assembly mounted for test in the Ram-Jet Facility is shown in Figure 43. A photograph showing the broken rear edge of the assembly after the test was stopped is shown in Figure 44.

The results of the tests on the leading edge assembly in the propane torch and ram-jet facilities indicates the coating is capable of withstanding oxidation and protecting the base metal along a leading edge under the severe conditions of re-entry for a glide re-entry vehicle.

CONCLUSIONS

1. Bend tests indicate the three alloys (Cb-1 Zr, C-103, and D-31) coated with either the Si-Cr-Al or the Si-Cr-B coatings systems may be bent at room temperature to a radius of 0.8" over a 1-1/2" length without visible failure. This minimum radius is believed to be adequate for flexing operations required in handling and fabricating assemblies of the coated sheet materials.

2. Load cycle tests indicate the ability of the coated thin sheet (0.020") columbium alloys to withstand thermal cycling to 2500°F under sustained load is highly dependent upon the stress level. This is shown by a comparison of specimens tested at loads of approximately 10% and 20% of the ultimate strength at 2500°F. Specimens which were thermally cycled at 10% of ultimate withstood almost twice as many cycles as specimens stressed at 20% of ultimate. This effect appears to be related to the creep characteristics of the alloys. However, the Si-Cr-Al and Si-Cr-B coatings systems had sufficient ductility to protect the alloys well past the usual 0.2% elongation used in design of structures.

3. Optimization tests on the effects of process variables on oxidation resistance of the Si-Cr-Al and Si-Cr-B systems indicated the following conditions as being optimum:

<u>Process Variable</u>	<u>Si First Coat</u>	<u>Cr-Al or Cr-B Second Coat</u>
Temperature	2100°F	2200°F
Time	16 hours	16 hours
Pack Density	Unvibrated	Unvibrated
Pack Particle Size	fine (325 mesh)	fine (325 mesh)
Retort Seal Permeability	low	high
Halide Content	6 to 10%	4%

4. The most oxidation resistant coating for 2600°F was found to be the Si-Cr-B system deposited under the conditions shown in Item 3. Three identical sets of specimens with the two coating systems were prepared and tested with the following results:

<u>Alloy</u>	<u>Si-Cr-Al system</u>		<u>Si-Cr-B system</u>	
	<u>Hours at 2600°F without failure</u>	<u>Max. Average (9 specimens)</u>	<u>Hours at 2600°F without failure</u>	<u>Max. Average (3)</u>
Cb-1 Zr	12	8.8	14	11.1
C-103	13	9.0	15	11.4
D-31	12	10.9	15	11.4

5. Recent literature on silicide coatings for tungsten and molybdenum reported a destructive low temperature oxidation effect termed "the disilicide pest." Low temperature effects between 1000° and 2000°F on the two coating systems were determined for the coatings systems. It was found that the Si-Cr-B system exhibited excellent resistance in this range, as well as at the higher temperatures. The Si-Cr-Al system was found to have relatively poor resistance at the lower temperatures, although the resistance at the higher temperatures was good.

6. Analytical evaluation, including X-ray diffraction and emission studies in conjunction with metallographic techniques, revealed the following information about the two coatings systems:

a. The formation of NbSi_2 appears to be at least a two-step process that is both time and temperature dependent, involving the formation of Nb_2Si_3 and subsequent recombinations to NbSi_2 .

b. Orientation of the NbSi_2 results from a long period of time at elevated temperature and permits crystal growth to proceed in the most desirable direction from the thermodynamic point of view, and this appears to be the (110).

c. The depth of penetration appears to be both a diffusion controlled and a reaction controlled mechanism, which tends to restrict the depth of penetration of the compounds formed in the Cr-Al and Cr-B coatings.

d. The compounds NbCr_2 , Cr_3Si , Al_2Cr_3 , Al_3Nb , $\text{Al}_{13}\text{Cr}_4\text{Si}_4$, and NbSi_2 were tentatively identified at various depths in the Si-Cr-Al coatings. However, no observations were made as which was the most active compound or compounds in affording oxidation resistance.

e. The compounds NbCr_2 , Cr_3Si , NbSi_2 , NbB_2 , and Fe_2B were tentatively identified at various depths in the Si-Cr-B coatings.

7. Various methods of fabricating and coating of columbium component parts were evaluated and the best oxidation resistance was obtained by using the following techniques:

a. Riveted components should be prepared by first forming and drilling all rivet holes. The drilled parts and rivets should be coated with the silicide coating. The parts are then riveted together and a second silicide coat should be deposited on the joined components. The Cr-Al or Cr-B should be deposited as a final coating.

b. Welded specimens containing coated butt welds, lap weld, and resistance spot welds were evaluated. The best oxidation resistance was obtained with the coated butt welds.

c. Bolt specimens with Wentworth threads were coated and a satisfactory fit of the nut on the bolt was obtained.

8. A simulated leading edge assembly (12" long) containing welds and rivets on the hot surface side of the structure was fabricated and coated with the Si-Cr-B system. This assembly was tested in the Vought Propane Torch and Ram-Jet Facilities under idealized re-entry conditions for a glide re-entry vehicle. The maximum temperature required in the re-entry cycle was 2350°F, with a maximum dynamic surface pressure of 800 pounds per square foot and a maximum sound level of 140 decibels. The simulated leading edge assembly satisfactorily exceeded the requirements of the idealized re-entry conditions. In these tests, a maximum temperature of 2500°F was reached with thirty minutes above 2000°F. The maximum sound level reached was 170 decibels (10 times the sound energy level required) and a maximum dynamic surface pressure of 1200 pounds per square foot. At this sound and surface pressure level, the assembly experienced a structural failure on a one-inch width unsupported edge. There was no evidence of coating damage except along the broken edge.

TABLE 1.
ANALYSIS OF ALLOYS RECEIVED FOR COATING*

ALLOY	Cb-1 Zr		C 103	D 31
SOURCE	Wah Chang		Wah Chang	duPont
HEAT	8-2033	82199	3.54.5 - 744	31-007
				Analysis
Ingot Analysis				
Composition, Per Cent				
Top	Bottom	Top	Bottom	
Cb	98.7%	98.9%	Cb	99.0%
Zr	1.20%	1.00%	Zr	0.88%
Impurity Content, PPM				
Top	Bottom	Top	Bottom	
C	<30	<30	Al	<20
N	130	130	B	<1
O	280	280	C	51
H	0.8	1.3	Cd	<5
B	<1	<1	Ge	<20
Cd	<5	<5	Cr	<20
CO	<20	<20	Cu	<40
Hf	<80	<80	Fe	<100
Fe	<100	<100	H	2.0
Pb	<20	<20	Hf	<80
Mn	20	20	Mg	<20
Mo	25	20	Mn	<20
Ni	<20	<20	Mo	<20
Si	<100	<100	N	82
Ta	430	<300	Ni	<20
Ti	<150	<150	O	270
W	<300	<300	Pb	<20
V	<20	<20	Si	<100
R.E.	<100	<100	Sn	<20

CONTINUED

TABLE 1.
ANALYSIS OF ALLOYS RECEIVED FOR COATING*(Continued)

ALLOY	Cb-1 Zr	C 103	D 31
SOURCE	Wah Chang	Wah Chang	duPont
HEAT	8-2033	82199	31-007
		3.54.5 - 74.4	
<u>Hardness in BHN</u>		<u>Hardness in BHN</u>	
Average	102.5	Average	105
Range	96.3 - 109	Range	100 - 109
<u>Product Analysis, PPM</u>			
Cb	98.5%		
Zr	1.0%		
C	30		
H	1.0		
N	110		
O	260		
<u>Hardness</u>			
Average R _B	82		

*Certified analysis by source

TABLE 2.
STRENGTH OF REPRESENTATIVE COLUMBIUM ALLOYS
Reference 4

Alloy	Crystallization Temp. (1 Hr.)	Room Temp.			1600°F			2000°F			2200°F			2400°F			2500°F		
		UTS	YS	% El.	UTS	YS	% El.	UTS	YS	% El.	UTS	YS	% El.	UTS	YS	% El.	UTS	YS	% El.
G.E. F48	2300°F	122	110	16				65	43	19	40	37	41	31	29		27	47	
G.E. F50	2500°F	122	30	24				50	34	28	35	27	35	21	17	45			
Fansteel FS-80	2200°F	60	46	17				14		10									
Fansteel FS-82	2200°F	82	70	11	65	52	7	45	40	8	10	7	80				12	11	53
Fansteel S-83											38	34	16				26	23	28
duPont D-31	2200°F	100	92	22				34	33	12	25	22	14	17		8			
duPont D-41		125		10				50		25	45			30					
duPont D-42								85			55								
Westinghouse NC-31		103	100	17				43	34	5									
Westinghouse NC-32		77	54	26				49	46	25									
Wah Chang C-103	Cold Rolled	105	97	11				43	24	39							13	11	87
Wah Chang C-103	Recrystallized	56	42	33				27	18	45							12	10	92
Wah Chang Cb-1 Zr	2200°F	47		20				13		10									

TABLE 3

ROOM TEMPERATURE STRENGTH OF 0.020"¹
COATED AND UNCOATED COLUMBIUM ALLOYS¹

Alloy	Coating	.2% Yield Strength, psi	Ultimate Strength, psi	% Elong. Over 2"
Cb-1 Zr	None	28,200	48,900	16
	None	28,200	46,900	18
D-31	None	136,000	157,200	3.0
	None	131,900	157,300	5.0
C-103	None	Avg. 133,950	Avg. 157,250	Avg. 4.0
		107,400	116,000	3.0
		112,400	118,700	
		Avg. 109,900	Avg. 117,350	Avg. 3.5

NOTES: ¹Specimens as shown in Figure 1

TABLE 4
PHASE I - OXIDATION RESISTANCE TESTS ON COATED CB-1 Zr SPECIMENS

Deposited Component of Coated Material		Oxidation Exposure		Average Specimen Wt. Increase (3 Specimens) mg/cm ² /Hr.	Mode of Oxidation Failure
First Cycle	Second Cycle	Time	Temp. of		
60% Si	40% Cr 20% B	5-1/2	2300	.32	Slight edge failure
30% Cr 30% Al	60% Si	1/2	2600	----	Coating melted
60% Si	50% Cr	1/2	2600	2.4	Destroyed by melted coating from adjacent specimens
50% Si 10% Al	None	1/2	2600	----	Coating melted
60% Si	None	1/2	2300	----	Coating melted
55% Si 5% Y	30% Cr 30% Al	4	2300	1.1	Small blister formed - oxidation underneath
20% B	60% Si	1/2	2300	----	Coating melted
60% Si	30% FeB 30% Cr.	5-1/2 3	2300 2600	1.8	Slight oxidation along edge of specimens (Si-Cr-B system)
60% Si	35% Cr 20% Al	5	2600	1.0	Slight oxidation along edge of specimens (Si-Cr-Al system)
60% Si	25% Cr 25% Al	2	2600	1.48	Edge Failure

Note 1. Balance of pack consisted of Al₂O₃ and halides.

Note 2. All coatings were made in furnace at 1900° ± 25°F for 16 hours.

TABLE 5

PHASE I OXIDATION RESISTANCE TESTS ON
COATED SPECIMENS BEFORE OPTIMIZATION OF COATING SYSTEMS

Alloy	Deposited Component of Coated Material		Oxidation Exposure		Average Specimen Weight Increase (Average of Three Specimens mg/cm ² /hr)
	1st Cycle	2nd Cycle	Average Time Hrs	Temp. °F	
Cb-1 Zr	Si	Cr-Al	5	2600	1.0
Cb-1 Zr	Si	Cr-B	5-1/2	2300	1.8
			3	2600	
C-103	Si	Cr-Al	4-1/2	2600	3.3
C-103	Si	Cr-B	4	2600	6.0
D-31	Si	Cr-Al	5	2600	3.1
D-31	Si	Cr-B	4	2600	2.3

Notes: 1. Balance of pack in each cycle consisted of Al_2O_3 and halides.
2. All coatings were deposited at $1900^{\circ} \pm 25^{\circ}F$ for 16 hours.

TABLE 6

TENSILE STRENGTH OF 0.020" THICK
COATED COLUMBIUM ALLOYS¹ AT VARIOUS TEMPERATURES

Alloy	Test Temp. °F	Coating ²	Ult. Tensile Strength, psi
Cb-1 Zr	75	Si-Cr-Al	49,200
Cb-1 Zr	75	Si-Cr-Al	49,400
Cb-1 Zr	75	Si-Cr-B	49,800
Cb-1 Zr	75	Si-Cr-B	50,300
Cb-1 Zr	2000	Si-Cr-Al	13,700
Cb-1 Zr	2000	Si-Cr-Al	13,300
Cb-1 Zr	2000	Si-Cr-B	13,200
Cb-1 Zr	2000	Si-Cr-B	13,400
D-31	2500	Si-Cr-Al	11,100
D-31	2500	Si-Cr Al	10,700
D-31	2500	Si-Cr-B	11,000
D-31	2500	Si-Cr-B	10,600
C-103	2500	Si-Cr-Al	11,700
C-103	2500	Si-Cr-Al	10,900
C-103	2500	Si-Cr-B	11,200
C-103	2500	Si-Cr-B	11,600

NOTES: ¹Transverse specimens, machined as shown in
Figure 1

²Coatings deposited on specimens in two cycles
Si first coat at 1900°F for 16 hours
Cr-Al or Cr-B second coat at 1900°F
for 16 hours

TABLE 7

STATIC LOAD TESTS AT 2500°F ON
COATED COLUMBIUM ALLOY SPECIMENS¹

Alloy	Coating ²	Test Temp.	Static Load	Elong. Over 2" Lgth. After Seven Minutes at Temp., %
D-31	Si-Cr-B	2500	6500	38
D-31	Si-Cr-B	2500	1000	1.0
D-31	Si-Cr-B	2500	2000	1.0
D-31	Si-Cr-B	2500	3000	1.5
D-31	Si-Cr-B	2500	4000	2.5
D-31	Si-Cr-Al	2500	1000	.5
D-31	Si-Cr-Al	2500	2000	.5
D-31	Si-Cr-Al	2500	3000	Premature failure
C-103	Si-Cr-B	2500	1000	.5
C-103	Si-Cr-B	2500	5000	17.5
C-103	Si-Cr-Al	2500	1000	1.0

NOTES: ¹Tensile specimens machined as shown in Figure 1

²Coatings deposited on specimens in two cycles
Si first coat at 1900°F for 16 hours
Cr-Al or Cr-B second coat at 1900°F for 16 hours

TABLE 8
 LOAD CYCLE TESTS ON COATED
 COLUMBIUM ALLOY TENSILE SPECIMENS¹

Alloy	Coating ²	Static Load psi	Load Cycles Completed
Cb-1 Zr	Si-Cr-Al	2000	3
Cb-1 Zr	Si-Cr-B	2000	2
Cb-1 Zr	Si-Cr-Al	1000	5
Cb-1 Zr	Si-Cr-Al	1000	6
Cb-1 Zr	Si-Cr-B	1000	6
Cb-1 Zr	Si-Cr-B	1000	3
			Avg. 5
C-103	Si-Cr-B	2000	2 ³
C-103	Si-Cr-B	2000	6
C-103	Si-Cr-Al	2000	2
			Avg. 5
C-103	Si-Cr-B	1000	18
C-103	Si-Cr-Al	1000	11
C-103	Si-Cr-Al	1000	9
			Avg. 13
D-31	Si-Cr-B	2000	7
D-31	Si-Cr-Al	2000	7
			Avg. 7
D-31	Si-Cr-B	1000	15
D-31	Si-Cr-B	1000	12
D-31	Si-Cr-Al	1000	12
D-31	Si-Cr-Al	1000	23
			Avg. 15

NOTES: ¹Transverse specimens, machined as shown in Figure 1

²Coatings deposited on specimens in two cycles:
 Si first coat at 1900°F for 16 hours
 Cr-Al or Cr-B second coat at 1900°F for 16 hours

³Imperfection in base metal

TABLE 9

RESULTS OF BEND TESTS ON COATED 0.020" SPECIMENS¹ OF
Cb-1 Zr, D-31, AND C-103

Alloy	Coating ²	Test Temp °F	Extent of Bend at Failure ³		Mode of Failure
			Bend Angle	Radius Inch	
Cb-1 Zr	None	75	180°	0.5	No failure
Cb-1 Zr	None	75	180°	0.5	No failure
Cb-1 Zr	None	75	180°	0.5	No failure
Cb-1 Zr	Si-Cr-Al	75	180°	0.5	Coating flaked off in straight line
Cb-1 Zr	Si-Cr-Al	75	157°	0.57	Coating flaked off in straight line
Cb-1 Zr	Si-Cr-Al	75	157°	0.57	Coating flaked off in straight line
Cb-1 Zr	Si-Cr-B	75	112°	0.8	Coating flaked off in straight line
Cb-1 Zr	Si-Cr-B	75	180°	0.5	Coating flaked off in straight line
Cb-1 Zr	Si-Cr-B	75	112°	0.8	Coating flaked off in straight line
Cb-1 Zr	None	-100	180°	0.5	No failure
Cb-1 Zr	None	-100	180°	0.5	No failure
Cb-1 Zr	None	-100	180°	0.5	No failure
Cb-1 Zr	Si-Cr-Al	-100	90°	1.0	Specimen broke without prior effect on coating
Cb-1 Zr	Si-Cr-Al	-100	90°	1.0	Specimen broke without prior effect on coating
Cb-1 Zr	Si-Cr-Al	-100	90°	1.0	Specimen broke without prior effect on coating
Cb-1 Zr	Si-Cr-B	-100	90°	1.0	Specimen broke without prior effect on coating
Cb-1 Zr	Si-Cr-B	-100	90°	1.0	Specimen broke without prior effect on coating
Cb-1 Zr	Si-Cr-B	-100	112°	0.8	Specimen broke without prior effect on coating

CONTINUED

TABLE 9
(CONTINUED)

Alloy	Coating ²	Test Temp °F	Extent of Bend at Failure ³		Mode of Failure
			Bend Angle	Radius Inch	
5	D-31	None	75	180°	0.5
	D-31	None	75	180°	0.5
	D-31	None	75	180°	0.5
	D-31	Si-Cr-Al	75	135°	0.65
	D-31	Si-Cr-Al	75	112°	0.8
	D-31	Si-Cr-Al	75	90°	1.0
	D-31	Si-Cr-B	75	90°	1.0
	D-31	Si-Cr-B	75	90°	1.0
	D-31	Si-Cr-B	75	112°	0.8
	D-31	None	-100	180°	0.5
	D-31	None	-100	135°	0.66
	D-31	None	-100	180°	0.5
	D-31	Si-Cr-Al	-100	90°	1.0
	D-31	Si-Cr-Al	-100	112°	0.8
	D-31	Si-Cr-Al	-100	112°	0.8
	D-31	Si-Cr-B	-100	112°	0.8
	D-31	Si-Cr-B	-100	112°	0.8
	D-31	Si-Cr-B	-100	112°	0.8

CONTINUED

TABLE 9
(Continued)

Alloy	Coating ²	Test Temp. °F	Extent of Bend at Failure ³		Mode of Failure
			Bend Angle	Radius Inch	
C-103	None	75	180	0.5	No failure
C-103	None	75	180	0.5	No failure
C-103	None	75	180	0.5	No failure
C-103	Si-Cr-Al	75	157	0.57	Coating flaked off in straight line
C-103	Si-Cr-Al	75	135	0.66	Coating flaked off in straight line
C-103	Si-Cr-Al	75	180	0.5	No failure
C-103	Si-Cr-B	75	135	0.66	Coating flaked off in straight line
C-103	Si-Cr-B	75	157	0.57	Coating flaked off in straight line
C-103	Si-Cr-B	75	180	0.5	No failure
C-103	None	-100	180	0.5	No failure
C-103	None	-100	180	0.5	No failure
C-103	None	-100	180	0.5	No failure
C-103	Si-Cr-Al	-100	157	0.57	Coating flaked off in straight line
C-103	Si-Cr-Al	-100	180	0.5	Slight flaking off of coating along edges
C-103	Si-Cr-Al	-100	180	0.5	Slight flaking off of coating along edges
C-103	Si-Cr-B	-100	135	0.66	Coating flaked off in straight line
C-103	Si-Cr-B	-100	180	0.5	Coating flaked off in straight line
C-103	Si-Cr-B	-100	157	0.57	Coating flaked off in straight line

NOTE: 1 Specimens prepared as shown in Figure 1

2 Coatings deposited on specimens in two cycles - Si first coat at 1900°F for 16 hours

Cr-Al or Cr-B second coat at 1900°F for 16 hours

3 Bend radius of 1-1/2" length of specimen

TABLE 10

EFFECT OF VARIATIONS OF RETORT SEAL PERMEABILITY AND COATING DEPOSITION TEMPERATURE ON COATING THICKNESSES AND OXIDATION RESISTANCE FOR Cb-12r SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM

Retort Seal Permeability ¹		Process Temp. (Both Cycles) OF	Coating Thick. Inches.	Initial Specimens		Replication Specimens	
				Avg. Exposure to Failure ²		Mode of Oxidation Failure	Avg. Exposure to Failure ²
				Hrs.	OF		
Low	Low	1700	.001	1	2400	Coating melted	1
Low	High	1700	.0009	1	2400	Face & edges	1
High	Low	1700	.001	1	2400	Face & edges	1
High	High	1700	.009	1	2400	Face	1
Low	Low	1900	.016	1	2500	Coating melted	1
Low	High	1900	.018	4	2600	Along edge	4
High	Low	1900	---	-	----	During processing	1
High	High	1900	---	1	2400	Face & edges	1
Low	Low	2100	.003	1	2500	Coating melted	1
Low	High	2100	.0039	8	2600	Along edges	6
High	Low	2100	.0041	1	2400	Along edges	1
High	High	2100	---	1	2400	Face & edges	1
Low	Low	2300	.005	1	2500	Coating melted	1
Low	High	2300	.006	1	2600	Along edges	1
High	Low	2300	---	-	----	During processing	-
High	High	2300	---	-	----	During processing	-

NOTES: ¹Retort seal permeability denotes permeability number of approximately 10 for low and 400 for high.

²Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F, and 2600°F until failure.

TABLE 11

EFFECT OF VARIATIONS OF RETORT SEAL PERMEABILITY AND COATING DEPOSITION TEMPERATURE ON COATING THICKNESS AND OXIDATION RESISTANCE FOR Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-B SYSTEM

Retort Seal Permeability ¹		Process Temp. (Both Cycles) °F	Coating Thick. Inches	Initial Specimens			Replication Specimens		
				Avg. Exposure to Failure ²		Mode of Oxidation Failure	Avg. Exposure to Failure ²		Mode of Oxidation Failure
				Hrs.	°F		Hrs.	°F	
Silicide	Cr-B								
1st Cycle	2nd Cycle								
Low	Low	1700	.0010	1	2400	General	-	-	Not Rerun
Low	High	1700	.0010	1	2600	Face & edges	-	-	Not rerun
High	Low	1700	.0012	1	2400	General	-	-	Not rerun
High	High	1700	.0013	1	2400	General	-	-	Not rerun
C3	Low	1900	.0018	1	2600	Coating melted	1	2600	Coating melted
	Low	1900	.0021	3	2600	Along edges	3	2600	Along edges
	High	1900	.0023	1	2500	Coating melted	-	-	Not rerun
	High	1900	.0020	1	2400	General	-	-	Not rerun
Low	Low	2100	.0035	1	2600	Coating melted	1	2600	Coating melted
Low	High	2100	.0047	4	2600	General	5	2600	Along edges
High	Low	2100	.0045	1	2600	General	-	-	Not rerun
High	High	2100	.0040	1	2500	General	-	-	Not rerun
Low	Low	2300	.0061	1	2600	Coating melted	1	2600	Coating melted
Low	High	2300	.0069	1	2400	Along edges	1	2500	Along edges
High	Low	2300	.0065	-	-	During processing	-	-	Not rerun
High	High	2300	.0064	-	-	During processing	-	-	Not rerun

NOTE: ¹Retort seal permeability denotes Permeability Number of approximately 40 for low and 400 for high.
²Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F and 2600°F until failure.

TABLE 12

EFFECT OF VARIATION OF Cr-Al SECOND COAT DEPOSITION TEMPERATURE AND TIME ON
 COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
 (SILICIDE FIRST COAT DEPOSITED AT 1700°F FOR 16 HOURS)

Cr-Al Second Coat Deposition Time and Temp. °F		Coating Thick. Inches	Initial Specimens				Replication Specimens	
			Avg.Exposure to Failure ¹		Mode of Oxidation Failure	Avg.Exposure to Failure ¹		Mode of Oxidation Failure
			°F	Hrs.		°F	Hrs.	
1700	10	.0007	2400	1	Face & edges	----	--	Not rerun
1700	16	.0008	2400	1	Face & edges	----	--	Not rerun
1700	22	.0008	2400	1	Face & edges	----	--	Not rerun
1900	10	.0007	2400	1	Face	----	--	Not rerun
1900	16	.0008	2400	1	Coating flaked off	----	--	Not rerun
1900	22	.0009	2400	1	Coating flaked off	----	--	Not rerun
2100	10	.0009	2400	1	Face	----	--	Not rerun
2100	16	.001	2500	1	Along edges	----	--	Not rerun
2100	22	.0009	2500	1	Along edges	----	--	Not rerun
2300	10	.001	2500	1	Along edges	----	--	Not rerun
2300	16	.001	2500	1	Along edges	----	--	Not rerun
2300	22	.0012	2500	1	Along edges	----	--	Not rerun

NOTE: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F, and 2600°F until failure.

TABLE 13

EFFECT OF VARIATION OF Cr-Al SECOND COAT DEPOSITION TEMPERATURE AND TIME ON
 COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
 (SILICIDE FIRST COAT DEPOSITED AT 1900°F FOR 16 HOURS)

Cr-Al Second Coat Deposition Temp. and Time		Coating Thick. Inches	Initial Specimens				Replication Specimens			
			Avg. Exposure to Failure ¹		Mode of Oxidation Failure		Avg. Exposure to Failure ¹		Mode of Oxidation Failure	
°F	Hours	Inches	Hours	°F			Hours	°F		
1700	10	.002	1	2500	Coating melted		-	----	Not rerun	
1700	16	.0019	2	2600			-	----	Not rerun	
1700	22	.002	2	2600			-	----	Not rerun	
1900	10	.0019	2	2600	Along edge		3	2600	Along edge	
1900	16	.002	4	2600			3	2600	Along edge	
1900	22	.002	4	2600			4	2600	Along edge	
2100	10	.0027	4	2600	Along edge		4	2600	Along edge	
2100	16	.0028	4	2600			5	2600	Along edge	
2100	22	.0031	5	2600			3	2600	Along edge	
2300	10	.003	5	2600	Along edge		5	2600	Along edge	
2300	16	.0035	7	2600			6	2600	Along edge	
2300	22	.004	7	2600			6	2600	Along edge	

NOTE: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F, and 2600°F until failure.

TABLE 14

EFFECT OF VARIATION OF Cr-Al SECOND COAT DEPOSITION TEMPERATURE AND TIME ON
COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
(SILICIDE FIRST COAT DEPOSITED AT 2100°F FOR 16 HOURS)

Cr-Al Second Coat Deposition Temp. and Time °F Hours		Coating Thick. Inches	Initial Specimens				Replication Specimens		
			Avg. Exposure ¹		Mode of Oxidation Failure	Avg. Exposure		Mode of Oxidation Failure	
			Hours	°F		Hours	°F		
1700	10	.0031	1	2500	Coating melted	-	-----	Not rerun	
1700	16	.0031	1	2600	Coating melted	-	-----	Not rerun	
1700	22	.0032	2	2600	Coating melted	-	-----	Not rerun	
1900	10	.0032	3	2600	Along edges	4	2600	Along edges	
1900	16	.0035	6	2600	Along edges	5	2600	Along edges	
1900	22	.0032	6	2600	Along edges	6	2600	Along edges	
2100	10	.0038	6	2600	Along edges	5	2600	Along edges	
2100	16	.0039	8	2600	Along edges	6	2600	Along edges	
2100	22	.0043	7	2600	Along edges	7	2600	Along edges	
2300	10	.0036	9	2600	Along edges	7	2600	Edges	
2300	16	.0040	10	2600	Test stopped	9	2600	Along edge	
2300	22	.0044	10	2600	Test stopped	10	2600	Test stopped	

NOTE: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F and 2600°F until failure.

TABLE 15

EFFECT OF VARIATION OF Cr-Al SECOND COAT DEPOSITION TEMPFRAURE AND TIME ON
 COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
 (SILICIDE FIRST COAT DEPOSITED AT 2300°F FCR 16 HOURS)

Cr-Al Second Coat Deposition Temp. and Time		Coating Thick. Inches	Initial Specimens			Replication Specimens			Mode of Oxidation Failure
			Avg.Exposure ¹		Mode of Oxidation Failure	Avg.Exposure ¹			
°F	Hrs.	°F	Hrs.	°F	Hrs.				
1700	10	.005	2500	1	Coating melted	----	--	Not rerun	Failure
	16	.005	2500	1	Coating melted	----	--	Not rerun	
	22	.006	2600	1	Coating melted	----	--	Not rerun	
	1900	.005	2400	1	Along edges	----	--	Not rerun	
	16	.005	2500	1	Along edges	----	--	Not rerun	
	22	.006	2600	2	Along edges	----	--	Not rerun	
	2100	.006	2500	1	Along edges	----	--	Not rerun	
	16	.007	2500	1	Along edges	----	--	Not rerun	
	22	.007	2600	1	Along edges	----	--	Not rerun	
2300	10	.006	2500	1	Along edges	----	--	Not rerun	Failure
	16	.006	2400	1	Along edges	----	--	Not rerun	
	22	.006	2500	1	Along edges	----	--	Not rerun	

NOTE: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, one hour at 2500°F, and 2600°F until failure.

TABLE 16

EFFECT OF VARIATION OF Cr-Al SECOND COAT DEPOSITION TEMPERATURE AND TIME ON
 COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-B SYSTEM
 (SILICIDE FIRST COAT DEPOSITED AT 1900°F for 16 HOURS)

Cr-Al Second Coat Deposition Temp. and Time		Coating Thick. Inches	Initial Specimens			Replication specimens		
			Avg. Exposure to Failure ¹	Mode of Oxidation Failure		Avg. Exposure to Failure ¹	Mode of Oxidation Failure	
°F	Hours	Inches	Hours	°F		Hours	°F	
1700	10	.0019	1	2600	Coating Melted	-	-	Not rerun
1700	16	.0020	1	2600	Coating Melted	-	-	Not rerun
1700	22	.0020	1	2600	Face	-	-	Not rerun
1900	10	.0021	2	2600	Face and Edge	3	2600	edge
1900	16	.0021	2	2600	Along Edge	2	2600	edge
1900	22	.0020	3	2600	Along Edge	3	2600	edge
2100	10	.0025	3	2600	Along Edge	3	2600	edge
2100	16	.0028	3	2600	Along Edge	4	2600	edge
2100	22	.0027	4	2600	Corner and Edge	4	2600	edge
2300	10	.0031	3	2600	Edge	3	2600	edge
2300	16	.0031	1	2600	Edge	-	-	Not rerun
2300	22	.0030	1	2600	Edge	-	-	Not rerun

Note: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F, One hour at 2500°F, and 2600°F until failure. Specimens cooled and inspected after each exposure.

TABLE 17

EFFECT OF VARIATION OF Cr-B SECOND COAT DEPOSITION TEMPERATURE AND TIME ON
 COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-B SYSTEM
 (SILICIDE FIRST COAT DEPOSITED AT 2100°F FOR 16 HOURS)

Cr-B Second Coat Deposition Temp. and Time	Coating Thick.	Initial Specimens				Replication Specimens		
		Avg. Exposure ¹		Mode of Oxidation Failure		Avg. Exposure	Mode of Oxidation	
°F	Hours	Inches	Hours	°F		Hours	°F	Failure
65	1700	.0040	1	2600	Coating melted	—	—	Not rerun
	1700	.0042	2	2600	Face	—	—	Not rerun
	1700	.0041	2	2600	Face	—	—	Not rerun
	1900	.0044	3	2600	Along edge	4	2600	Edges
	1900	.0043	3	2600	Along edge	4	2600	Along edge
	1900	.0045	2	2600	Along edge	4	2600	Edges
	2100	.0047	3	2600	Along edge	4	2600	Edges
	2100	.0047	4	2600	Along edge	5	2600	Edges
	2100	.0045	4	2600	Along edge	5	2600	Edges
	2300	.0060	7	2600	Edge and Corners	7	2600	Edges
	2300	.0062	8	2600	Face and edges	7	2600	Edges
	2300	.0055	3	2600	Severe on face and edges	2	2600	General

NOTE: ¹Oxidation specimens as in Figure 1. Exposure consisted of one hour at 2400°F and 2600°F until failure. Specimens cooled and inspected after each hour exposure.

TABLE 18

EFFECT OF VARIATION OF SILICIDE FIRST COAT DEPOSITION TEMPERATURE AND TIME ON
COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
(Cr-Al SECOND COAT DEPOSITED AT 2200°F FOR 16 HOURS)

Si First Coat Deposition Temp. and Time		Finished Coating Thick.	Initial Specimens			Replication Specimens		
			Avg. Exposure	Hours	Mode of Oxidation Failure	Avg. Exposure	Hours	Mode of Oxidation Failure
°F	Hours	Inches	Hours	°F		°F		
1900	10	.0024	4	2600	Face and edges	4	2600	Edges
1900	16	.0026	3	-----	Along edges	4	2600	Edges
1900	22	.0027	6	2600	Along edges	7	2600	Edges
2100	10	.0044	6	2600	Edges	5	2600	Edges
2100	16	.0045	10	2600	No failure-test stopped	9	2600	Face
2100	22	.0047	10	2600	No failure-test stopped	10	2600	No failure
2300	10	.0049	10	2600	No failure-test stopped	10	2600	Edge

NOTE: ¹Oxidation specimens as in Figure 1. Test consisted of one hour exposure until failure. After each hour specimens cooled to room temperature and examined.

TABLE 19

EFFECT OF VARIATION OF SILICIDE FIRST COAT DEPOSITION TEMPERATURE AND TIME ON
COATING THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-B SYSTEM
(Cr-B SECOND COAT DEPOSITED AT 2200°F FOR 16 HOURS)

Si First Coat Deposition Temp. and Time		Finished Coating Thick.	Initial Specimens			Replication Specimens		
			Avg. Exposure ¹	Hours	°F	Mode of Oxidation Failure	Avg. Exposure	Hours
1900	10	.0028	1	2600		Corners and edges	2	2600
1900	16	.0027	3	2600		Corners and edges	2	2600
1900	22	.0030	3	2600		Along edges	4	2600
2100	10	.0052	7	2600		Along edges	6	2600
2100	16	.0052	10	2600		No failure-test stopped	10	2600
2100	22	.0049	10	2600		No failure-test stopped	10	2600
2300	10	.0048	8	2600		Face and corner	10	2600

NOTE: ¹Oxidation specimens as in Figure 1. Test consisted of one hour exposures until failure. Specimens cooled to room temperature and examined after each hour.

TABLE 20

EFFECT OF PACK PARTICLE SIZE AND PACK DENSITY VARIATIONS ON COATING
 THICKNESS AND OXIDATION RESISTANCE OF Cb-12r SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
 (Silicide First Coat at 2100°F for 16 hours, Cr-Al at 2200°F for 16 hours)

Silicide 1st Coat		Cr-Al 2nd Coat		Coating Thick. Inches	Initial Specimens		Replication Specimens	
Alumina Particle Mesh Size	Pack Density Pounds Per Cu. In.	Alumina Particle Mesh Size	Pack Density Pounds Per Cu. In.		Oxidation Resistance at 2600°F Hours	Mode of Oxidation Failure	Oxidation Resistance at 2600°F Hours	Mode of Oxidation Failure
10-20 325	.0336	10-20	.0338	.0051	1	Face Edge & corners	1	Face Edge & corners
	.0309	10-20	.0338	.0047	5		4	
	.0325	10-20	.0338	.0058	1	Face & edges Along edges	1	Face Along edges
	.0299	10-20	.0338	.0050	7		5	
	.0336	325	.0322	.0054	4	Along edges	4	Face
	.0309	325	.0322	.0052	5	Edges & corners	8	Edges
	.0325	325	.0322	.0057	3	Face	3	Face & edges
	.0299	325	.0322	.0053	10	Slight on one edge	9	Edge
10-20 325	.0336	325	.0344	.0050	1	Face	1	Face
	.0309	325	.0344	.0048	10	Along edge	10	Slight on edge
	.0325	325	.0344	.0050	1	Face & edges	1	Face & edges
	.0299	325	.0344	.0046	9	Edges	10	No failure
	.0336	10-20	.0324	.0052	2	Face & edges	1	Face & edges
	.0309	10-20	.0324	.0053	5	Edges & corners	4	Edges
	.0325	10-20	.0324	.0055	4	Face & edges	4	
	.0299	10-20	.0324	.0050	5	Edges	6	Edges

TABLE 21

EFFECT OF VARIATION OF HALIDE CONTENT IN RETORT PACK MIX ON COATING
THICKNESS AND OXIDATION RESISTANCE OF Cb-1 Zr SPECIMENS COATED WITH THE Si-Cr-Al SYSTEM
(SILICIDE FIRST COAT DEPOSITED AT 2100°F FOR 16 HOURS Cr-Al SECOND COAT AT 2200°F FOR 16 HOURS)

Halide Content in Si Coating percent	Halide Content in Cr-Al Coating percent	Coating Thickness mils	Initial Specimens		Replication Specimens			
			Avg. Exposure to Failure Hours	°F.	Mode of Oxidation Failure	Avg. Exposure to Failure Hours	°F.	Mode of Oxidation Failure
63	6	4	5.4	7	2600 Edge	8	2600 Edge	Edge
	10	4	5.0	8	2600 Edge	8	2600 Edge	Edge
	14	4	4.7	6	2600 Edge	7	2600 Edge	Edge
	6	7	5.5	5	2600 Edge	5	2600 Edge	Edge
	10	7	5.1	6	2600 Edge	7	2600 Edge	Edge
	14	7	4.4	4	2600 Edge	4	2600 Edge	Edge
	6	10	4.9	3	2600 Face and edge	3	2600 Face and edge	Face and edge
	10	10	4.7	4	2600 Face and edge	4	2600 Face and edge	Face and edge
	14	10	5.0	3	2600 Face and edge	4	2600 Face and edge	Face and edge

NOTE: Specimens cooled and inspected after each hour exposure.

TABLE 22

RESULTS OF PHASE III OXIDATION TESTS AT 2600°F FOR DETERMINATION
OF RELIABILITY AND REPRODUCIBILITY OF THE
OPTIMIZED COATING SYSTEMS

Alloy	Coating System	Specimen Number	REPLICATION RUN 1		REPLICATION RUN 2		REPLICATION RUN 3	
			Exposure To Failure (Hours)	Mode of Oxidation Failure	Exposure To Failure (Hours)	Mode of Oxidation Failure	Exposure To Failure (Hours)	Mode of Oxidation Failure
Cb-1Zr	Si-Cr-Al	1	12	Edge & Corner	10	Corner	11	Corner
		2	7	Edge	7	Edge	8	Edge
		3	9	Edge	8	Edge	7	Edge
		Average:	9.3		8.3		8.7	
Cb-1Zr	Si-Cr-B	1	10	Edge	12	Edge	9	Face
		2	13	Corner	14	Face	10	Face
		3	11	Edge	11	Face	11	Face
		Average:	11.3		12.3		10	
C-103	Si-Cr-Al	1	8	Edge & Face	9	Edge	9	Edge
		2	13	Corner	7	Edge	9	Corner
		3	9	Edge	9	Edge	8	Corner
		Average:	10		8.3		8.7	
C-103	Si-Cr-B	1	8	Edge	12	Edge & Corner	15	Edge
		2	15	Corner	10	Edge & Corner	10	Face
		3	9	Corner	9	Edge & Corner	15	Edge
		Average:	10.7		10.3		13.3	
D-31	Si-Cr-Al	1	11	Edge	12	Corner	10	Edge
		2	8	Edge	11	Edge	12	Edge
		3	11	Edge	12	Edge	11	Corner
		Average:	10		11.7		11	
D-31	Si-Cr-B	1	8	Edge	13	Face	8	2.
		2	10	Face	9	Corner	15	Edge
		3	15	Edge	10	2.	12	Corner
		Average:	11		10.7		12.7	

NOTE: 1. Specimens were cooled and inspected after each hour of exposure at 2600°F.
2. Coating affected by failure of adjacent specimen during test.

TABLE 23

RESULTS OF LOW TEMPERATURE OXIDATION TESTS
ON OPTIMIZED COATINGS SYSTEMS¹

Alloy	Coating System	Specimen Number	REPLICATION RUN 1		REPLICATION RUN 2		REPLICATION RUN 3	
			Temperature At Failure °F	Mode of Oxidation Failure	Temperature At Failure °F	Mode of Oxidation Failure	Temperature At Failure °F	Mode of Oxidation Failure
Cb-1Zr	Si-Cr-Al	1	1400	Face	1400	Edge	1400	Edge & Face
		2	1400	Face	1400	Edge	1400	Edge & Face
Cb-1Zr	Si-Cr-B	1	1600	Edge	Full Cycle	-	Full Cycle	-
		2	Full Cycle	-	Full Cycle	-	Full Cycle	-
C-103	Si-Cr-Al	1	1400	Face	2000	Face	1400	Edge & Corner
		2	1400	Face	1400	Edge & Face	1400	Edge
C-103	Si-Cr-B	1	Full Cycle	-	Full Cycle	-	1800	Edge
		2	Full Cycle	-	Full Cycle	-	Full Cycle	-
D-31	Si-Cr-Al	1	1800	Edge	1800	Edge	2000	Edge
		2	1600	Edge	1800	Corner	1800	Corner
D-31	Si-Cr-B	1	Full Cycle	-	Full Cycle	-	Full Cycle	-
		2	Full Cycle	-	Full Cycle	-	Full Cycle	-

NOTE: 1. Test cycle consisted of successive one-hour exposures at the following temperatures: 2400, 1000, 1200, 1400, 1600, 1800, 2000 and 2400°F. Specimens were cooled and inspected after each hour of exposure.

TABLE 24

RESULTS OF OXIDATION BEND TESTS ON
OPTIMIZED COATING SYSTEMS¹

Alloy	Coating System	Specimen Number	REPLICATION RUN 1		REPLICATION RUN 2		REPLICATION RUN 3	
			Elongation At Failure Percent	Mode of Failure	Elongation At Failure Percent	Mode of Failure	Elongation At Failure Percent	Mode of Failure
Cb-14r	Si-Cr-Al	1	-	Damaged in handling.	1.0%	Oxidation on tension side.	1.0%	Oxidation on edge.
		2	<u>1.5%</u>	Edge oxidation.	<u>.5%</u>	Oxidation at edge.	<u>2.0%</u>	Oxidation on edge.
Cb-14r	Si-Cr-B	Average:	1.5%		.75%		1.5%	
		1	2.5%	Edge oxidation.	2.5%	Oxidation at edge.	2.0%	Oxidation on edge.
C-103	Si-Cr-Al	2	<u>2.5%</u>	Edge oxidation.	<u>2.5%</u>	No failure.	<u>2.5%</u>	No failure.
		Average:	2.5%	oxidation.	2.5%		2.2%	
C-103	Si-Cr-B	1	1.0%	Oxidation on tension side.	1.0%	Oxidation at edge.	2.0%	Oxidation on edge.
		2	<u>1.0%</u>	Oxidation at edge.	<u>1.0%</u>	Oxidation at edge.	<u>2.0%</u>	Oxidation on edge.
C-103	Si-Cr-B	Average:	1.0%	Oxidation at edge.	1.5%	Oxidation at edge.	2.0%	Oxidation on edge.
		1	1.5%					
D-31	Si-Cr-Al	2	<u>2.0%</u>	Oxidation at edge.	<u>1.5%</u>	Oxidation at edge.	<u>2.0%</u>	Oxidation along edge.
		Average:	1.7%	edge.	1.5%	edge.	2.0%	Oxidation on edge.
D-31	Si-Cr-B	1	.7%	Broke in bend fixture.	.9%	Broke in bend fixture.	1.0%	
		2	<u>.8%</u>	Broke in bend fixture.	<u>1.1%</u>	Broke in bend fixture.	<u>.9%</u>	Broke in bend fixture.
D-31	Si-Cr-B	Average:	.7%	1.0%	1.0%	Broke in bend fixture.	.9%	Broke in bend fixture.
		1	1.6%	Broke in bend fixture.	1.7%	Broke in bend fixture.	1.5%	Broke in bend fixture.
D-31	Si-Cr-B	2	<u>1.1%</u>	Broke in bend fixture.	<u>1.6%</u>	Broke in bend fixture.	<u>1.4%</u>	Broke in bend fixture.
		Average:	1.3%		1.5%		1.4%	

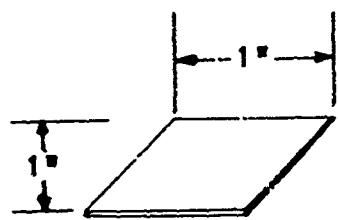
NOTE: 1. See Test Procedure Section for test method.
 2. Normal design requirements are based on 0.2% yield. All values shown above are well past point at which specimens took permanent set.

TABLE 25

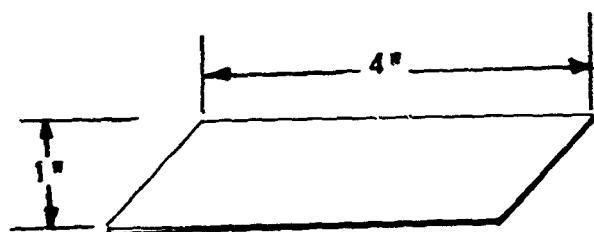
LAP SHEAR STRENGTH AT 2200°F OF RIVETED
SPECIMENS PREPARED BY THREE METHODS

Sequence of Preparation	Specimen Number	Load at Failure, lbs.	Remarks
Drill Holes/	1	148	Slight oxidation around rivets
Rivet/Si Coat/	2	67	Severe oxidation around one rivet
Cr-B Coat	3	102	Severe oxidation around one rivet
		Avg. <u>105</u>	
Si Coat/Drill	1	54	Severe oxidation around one rivet
Holes/rivet/	2	204	No evidence of oxidation
Si Coat/Cr-B Coat	3	172	Slight oxidation around rivets
		Avg. <u>143</u>	
Drill Holes/Si Coat/	1	380	No evidence of oxidation
Rivet/Si Coat/	2	215	No evidence of oxidation
Cr-B Coat	3	172	No evidence of oxidation
		Avg. <u>259</u>	

NOTE: Test consisted of heating specimens by radiant lamps to 2200°F and holding at temperature for five minutes. Specimens were then pulled at a load rate of 50 pounds per minute.



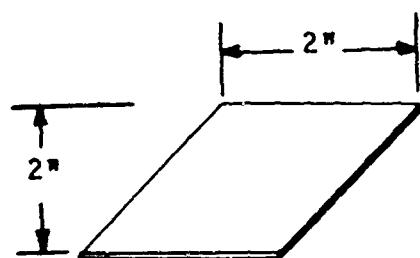
Oxidation Resistance



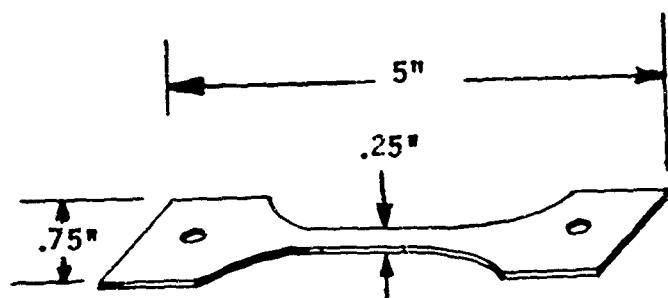
Transition Temperature
Bend



Metallurgical

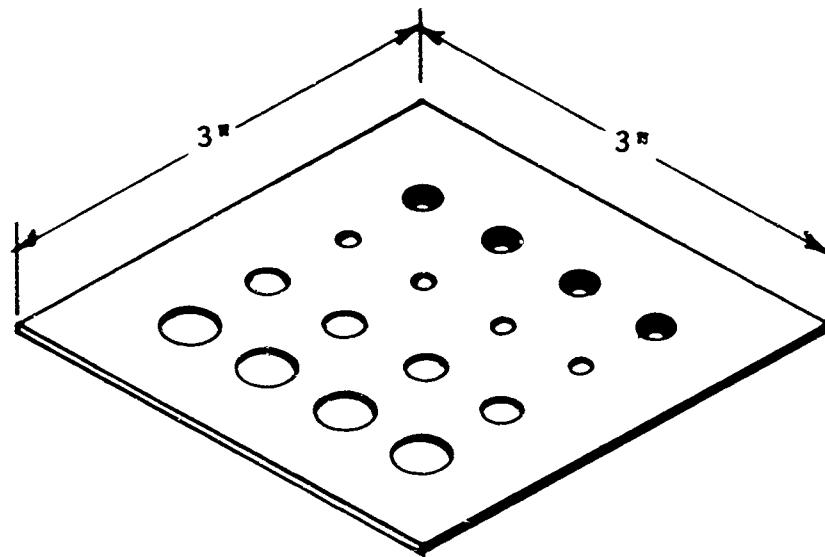


Emissivity

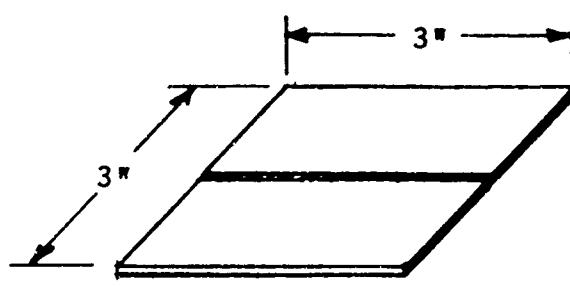


Tensile Strength
Load Cycle

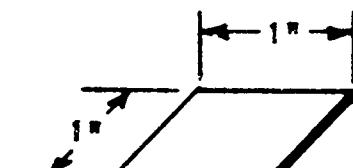
Figure 1 - Test Specimens Used in Phases I and II.
All Specimens 0.020" Nominal Thickness



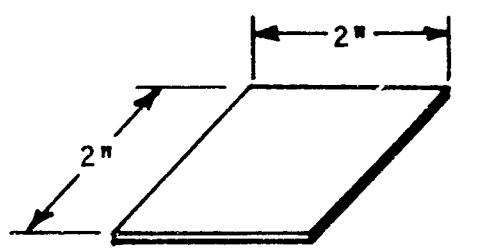
HOLE SIZE SPECIMEN



BUTT WELD SPECIMEN.



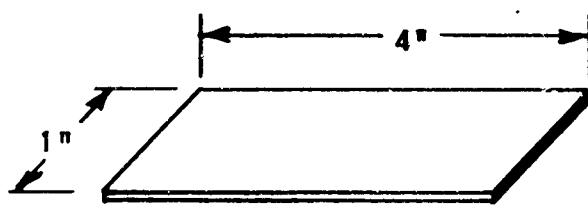
OXIDATION RESISTANCE



EMISSIVITY

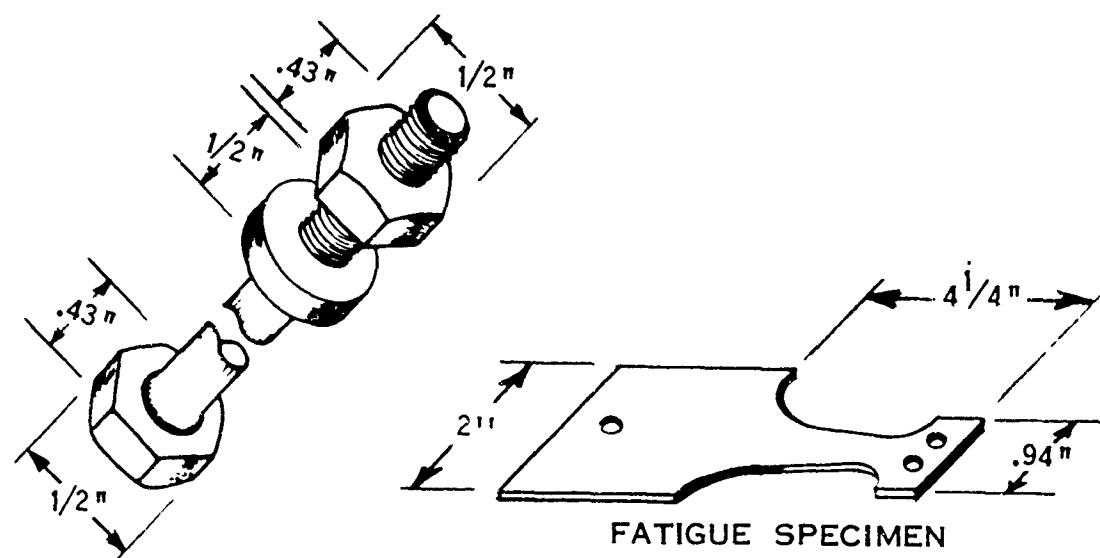
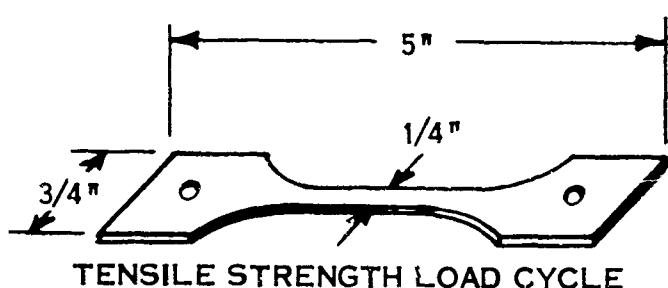
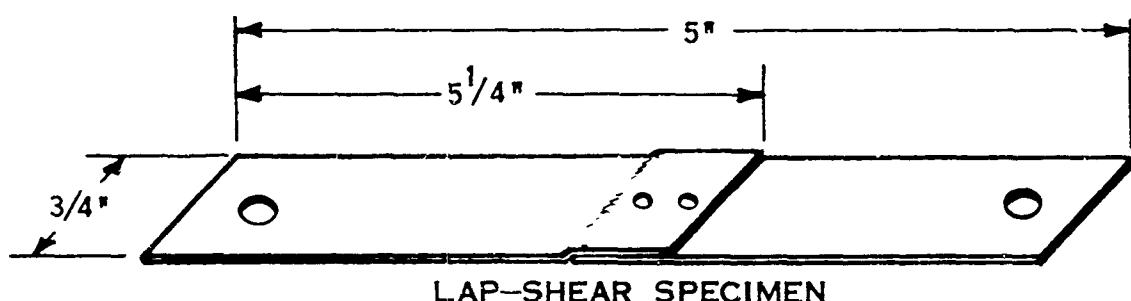
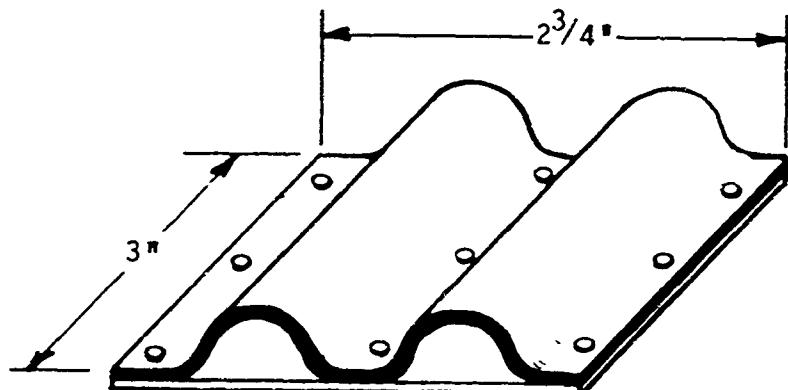


METALLURGICAL



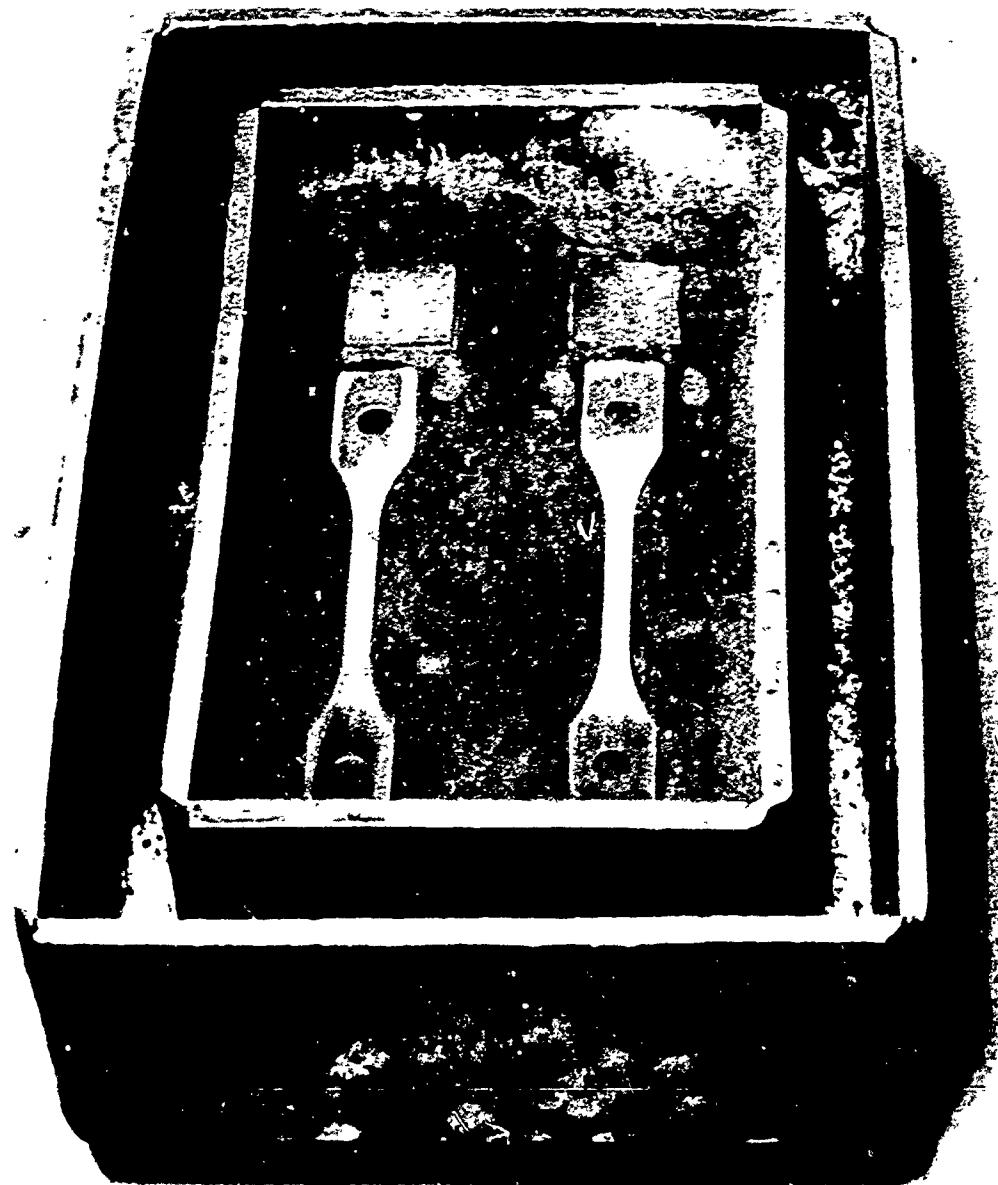
TRANSITION TEMPERATURE BEND

Figure 2 - Test Specimens Used in Phase III
All Specimens 0.020" Nominal Thickness



BOLT-WASHER-NUT SPECIMEN

Figure 2 - (Continued)



Shows tensile and oxidation resistance specimen placed on coating rack material

Figure 3 - Partially Loaded Retort



Figure 4 - Loading Retort in Furnace

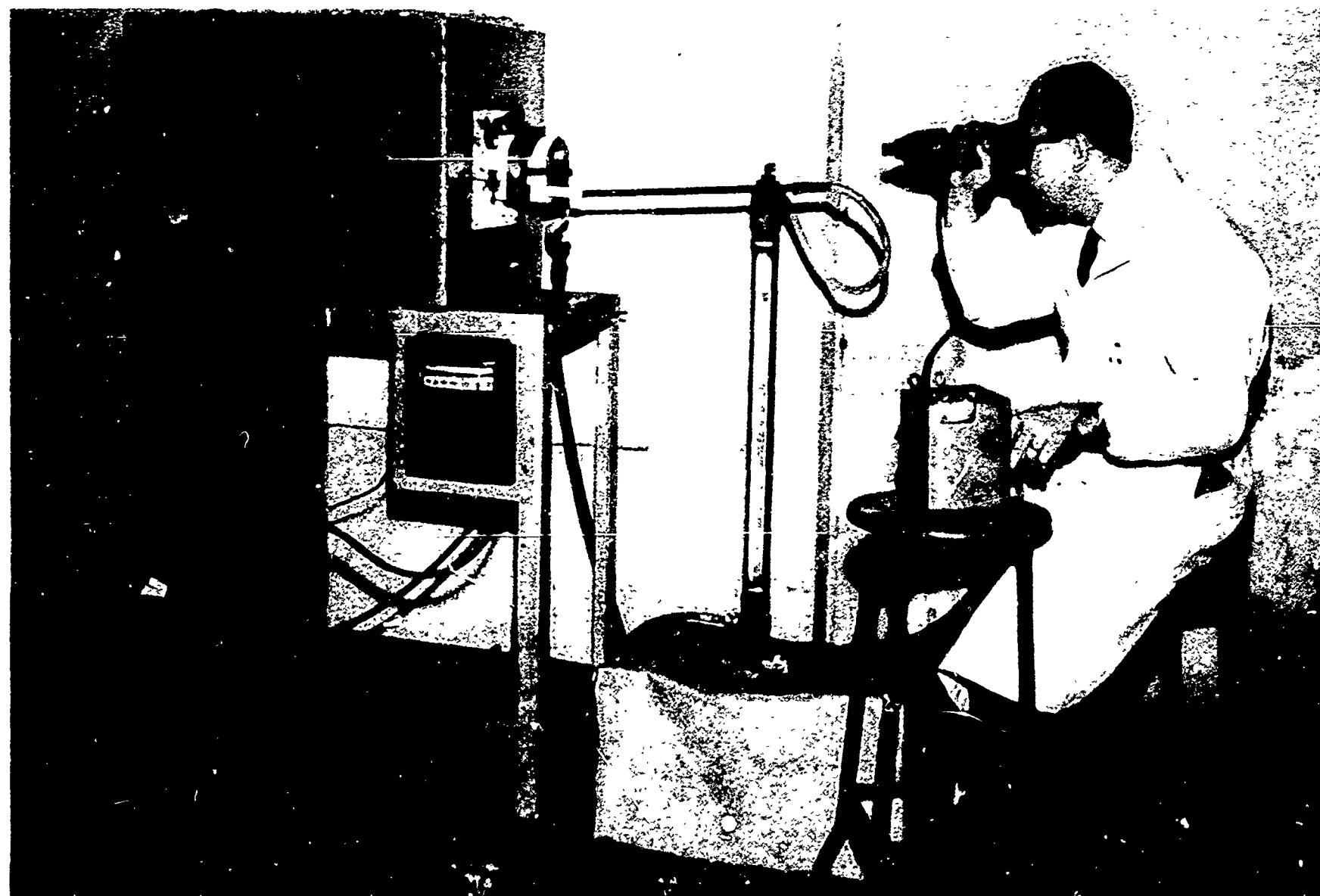


Figure 5 - Controlled Air Flow Furnace

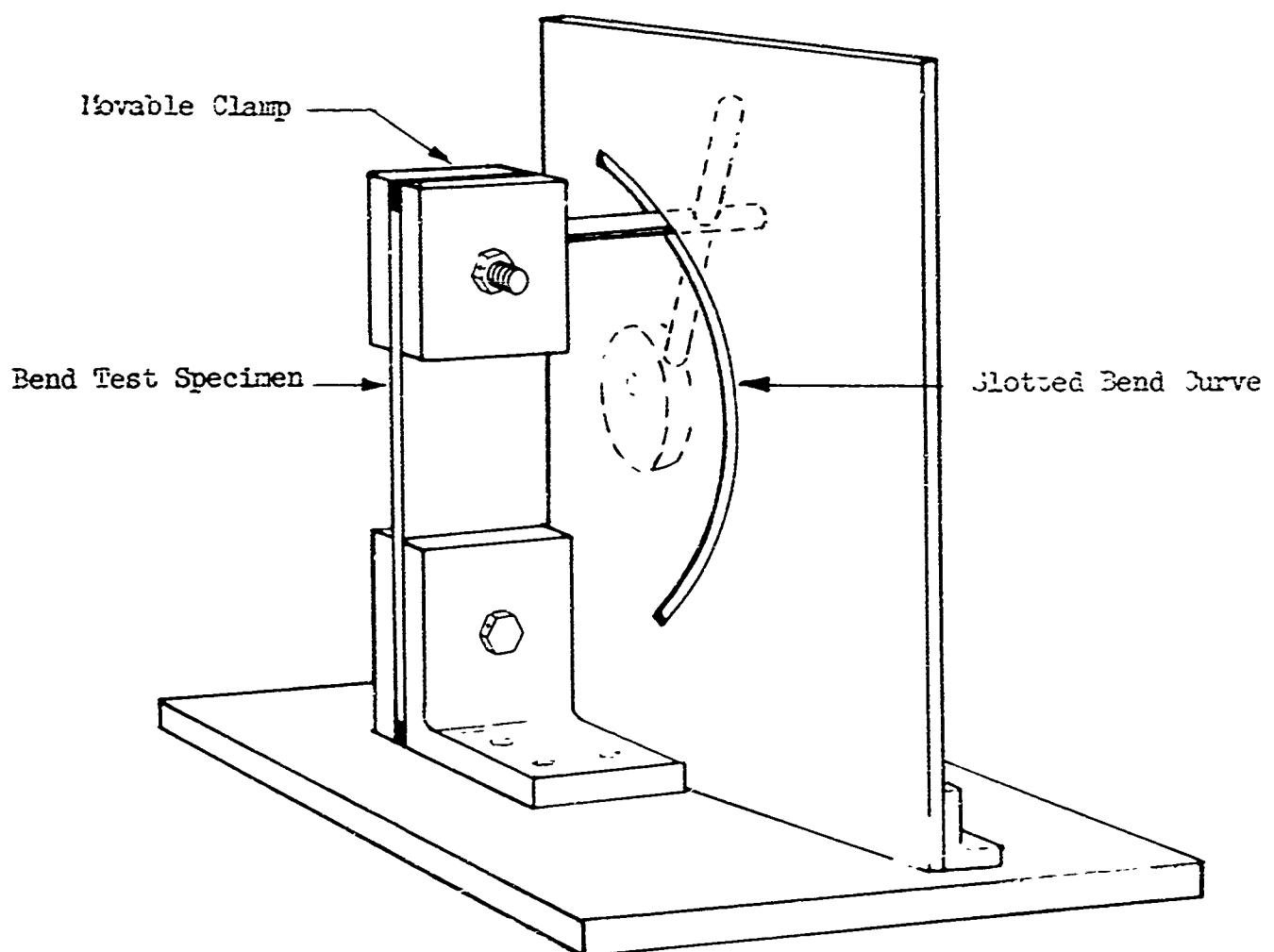


Figure 6 - Transition Temperature Bend Jig



Corner



Center



Corner

Figure 7 - Uncoated Cb-1 Zr (250X)



Corner



Center



Corner

Figure 8 - Uncoated D-31 (250X)



Corner



Center



Corner

Figure 9 - Uncoated C-103 (250X)



Figure 10 - Uncoated C-103 Showing an Inclusion in the Base Metal (250X)



Figure 11 - Cb-1 Zr Coated with Si-Cr-Al Deposited in Two Cycles.
1900°F for 16 Hours Each Cycle. (250X)

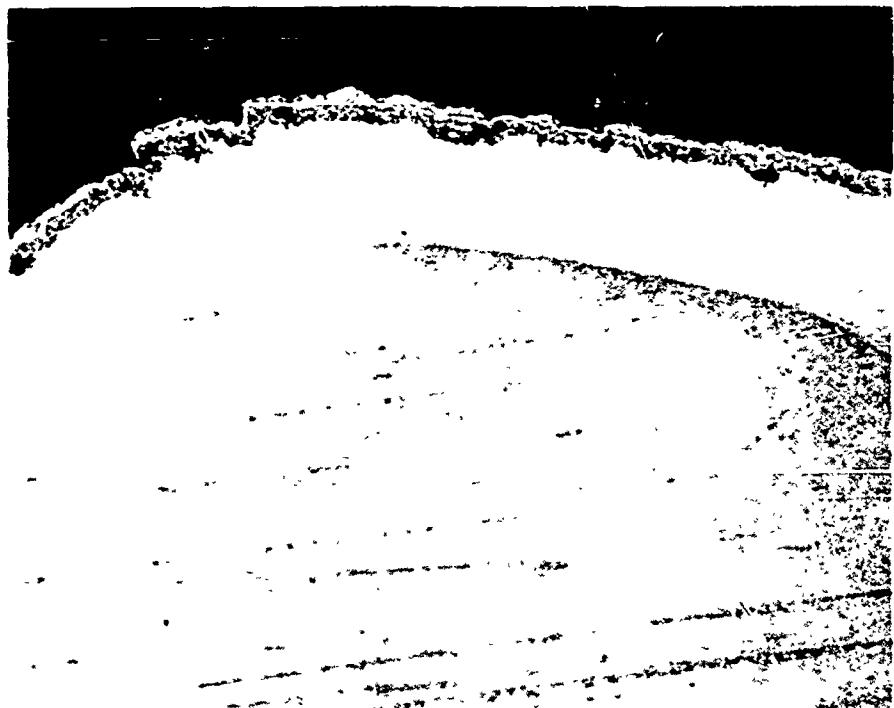
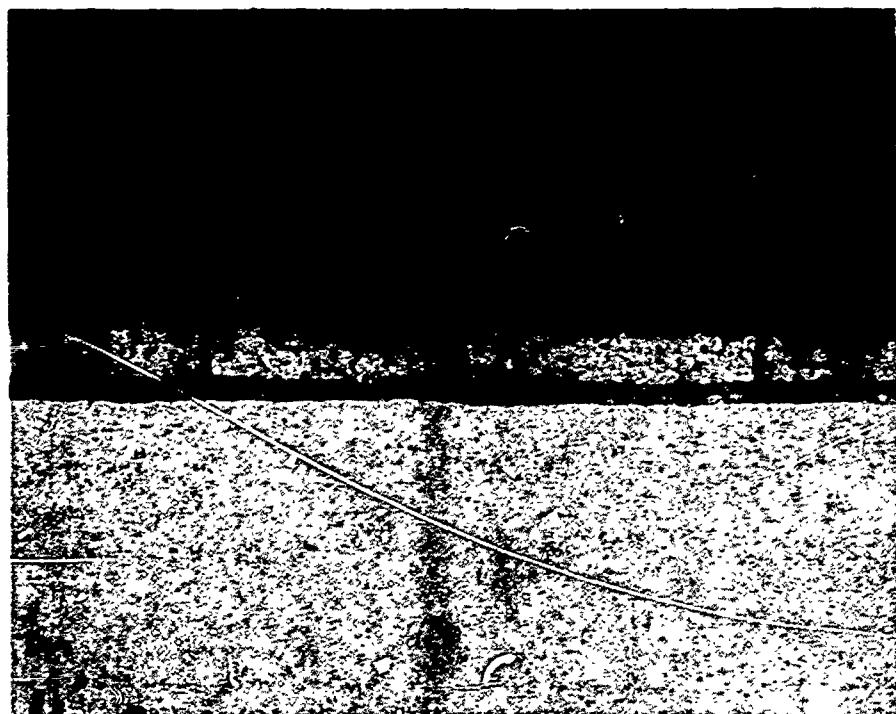
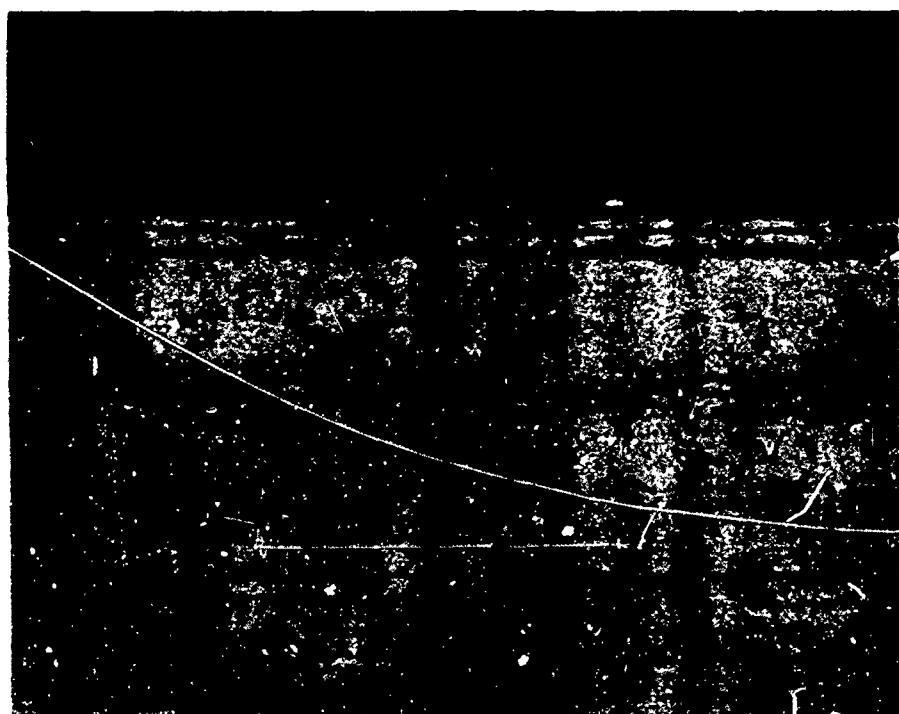


Figure 12 - Cb-1 Zr Coated with Si-Cr-B Deposited in Two Cycles.
1900°F for 16 Hours Each Cycle. (250X)



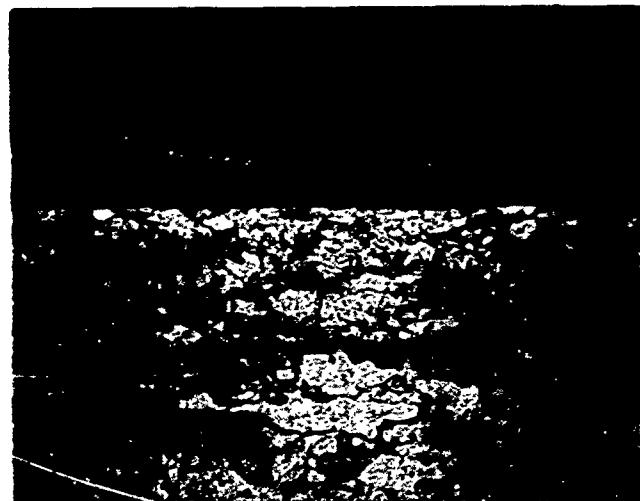
**Figure 13 - D-31 Coated with Si-Cr-Al Deposited in Two Cycles.
1900°F for 16 Hours Each Cycle. (250X)**



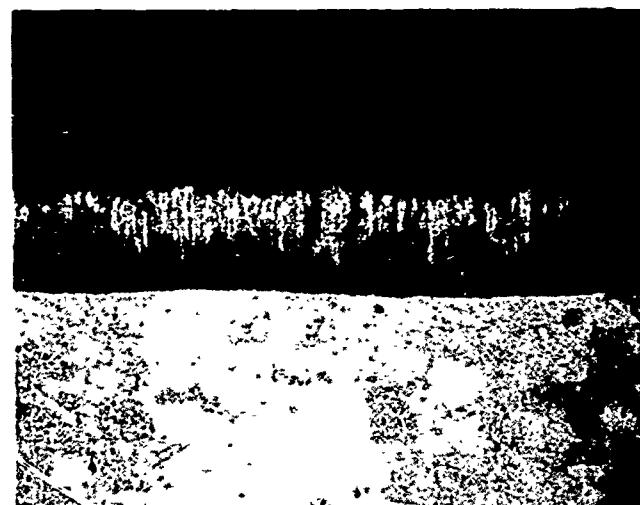
**Figure 14 - C-103 Coated with Si-Cr-Al Deposited in Two Cycles.
1900°F for 16 Hours Each Cycle. (250X)**



1700° F



1900° F



2100° F



2300° F

Figure 15 - Cb-1 Zr Coated with Si Only, at Various Temperatures for 16 Hours

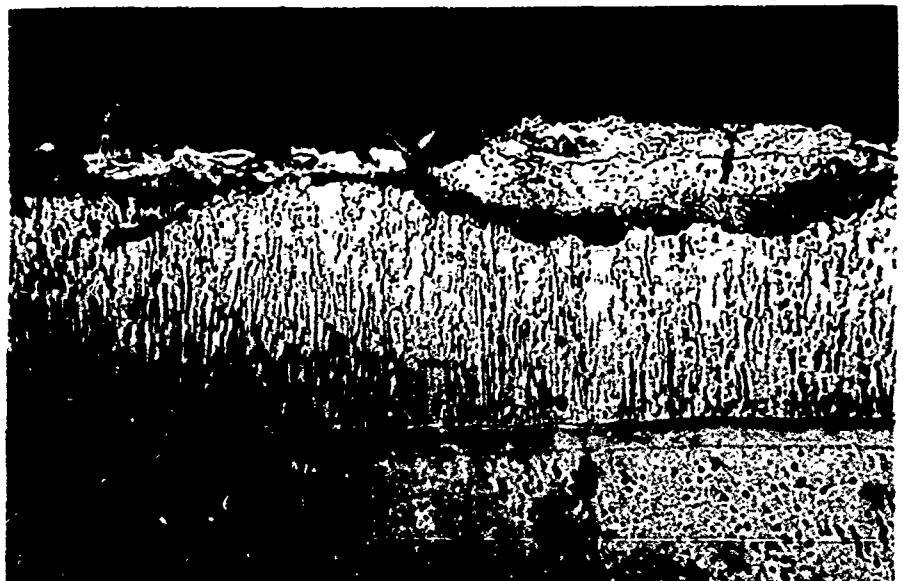
(a)

Silicide Coating Only Showing
Columnar Structure (250X)



(b)

Si-Cr-B Coating Deposited with
Low Permeability Retort Seal
for the Cr-B Pack



(c)

Si-Cr-B Coating Deposited with
High Permeability Retort Seal
for the Cr-B Pack



Figure 16 - Effect of Retort Seal Permeability on Deposition of
Cr-B on the Silicide Coating

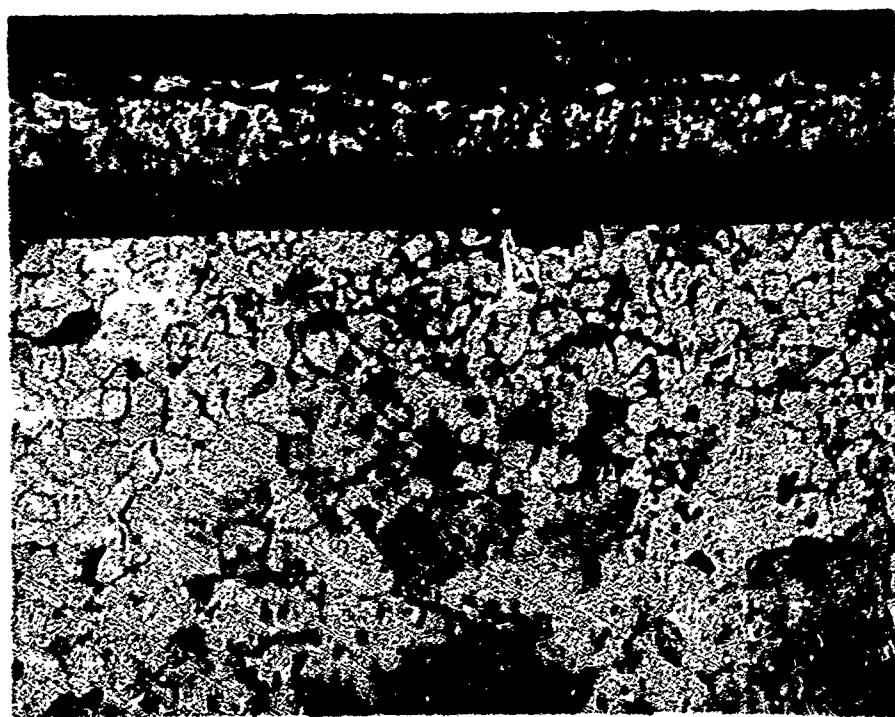


Cr-Al Second Coat Deposited at
1900°F for 16 Hours



Cr-Al Second Coat Deposited at
2100°F for 16 Hours

Figure 17 - Cr-Al Second Coats on Silicide Coatings Deposited at 1700°F on
Cb-1Zr (See Table 12) (250X)

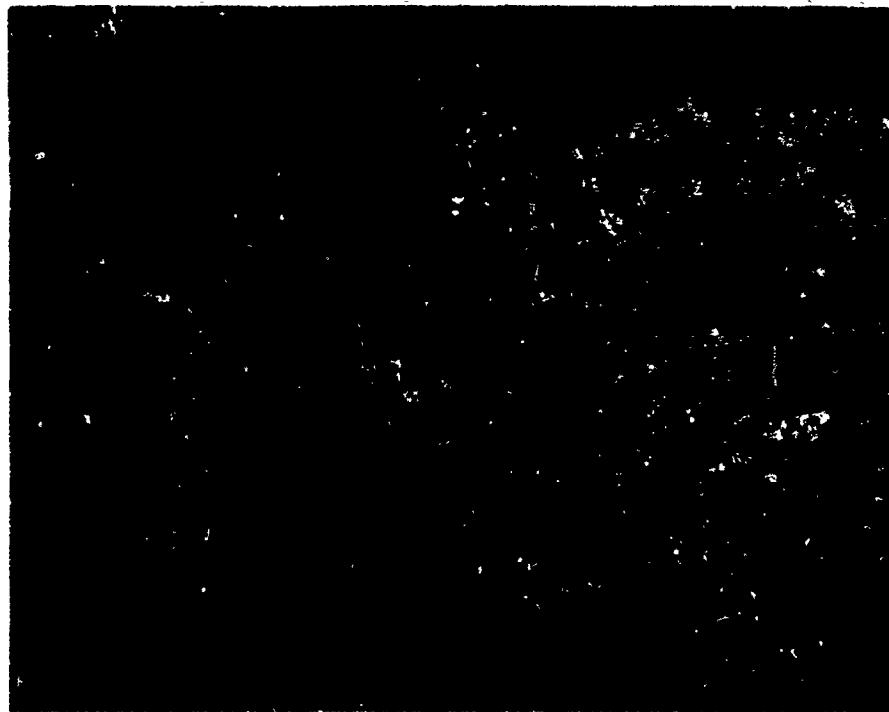


Cr-Al Second Coat Deposited at
2100°F for 16 Hours

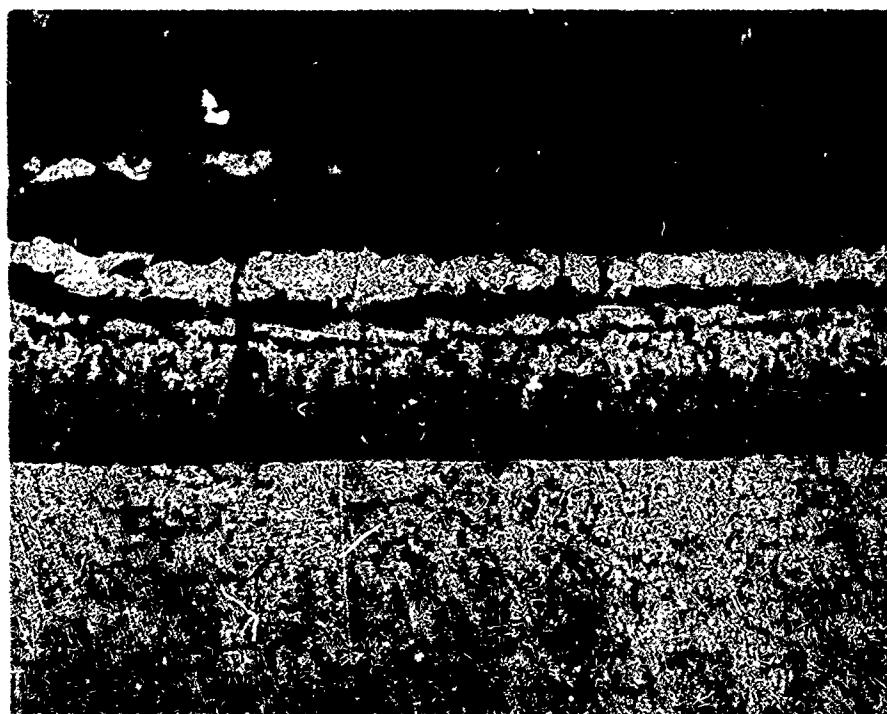


Cr-Al Second Coat Deposited at
2300°F for 16 Hours

Figure 18 - Cr-Al Second Coats on Silicide Coatings Deposited at 1900°F on Cb-1Zr (See Table 13) (250X)

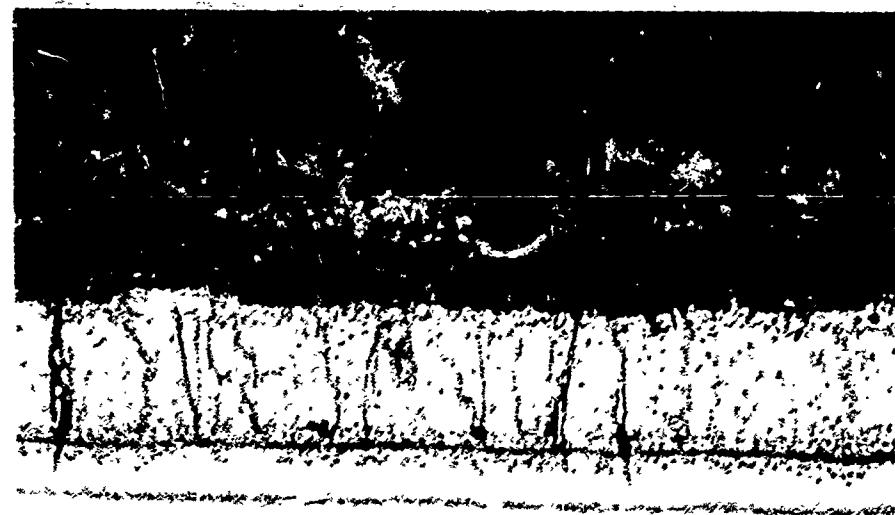


Cr-Al Second Coat Deposited at
2100°F for 16 Hours



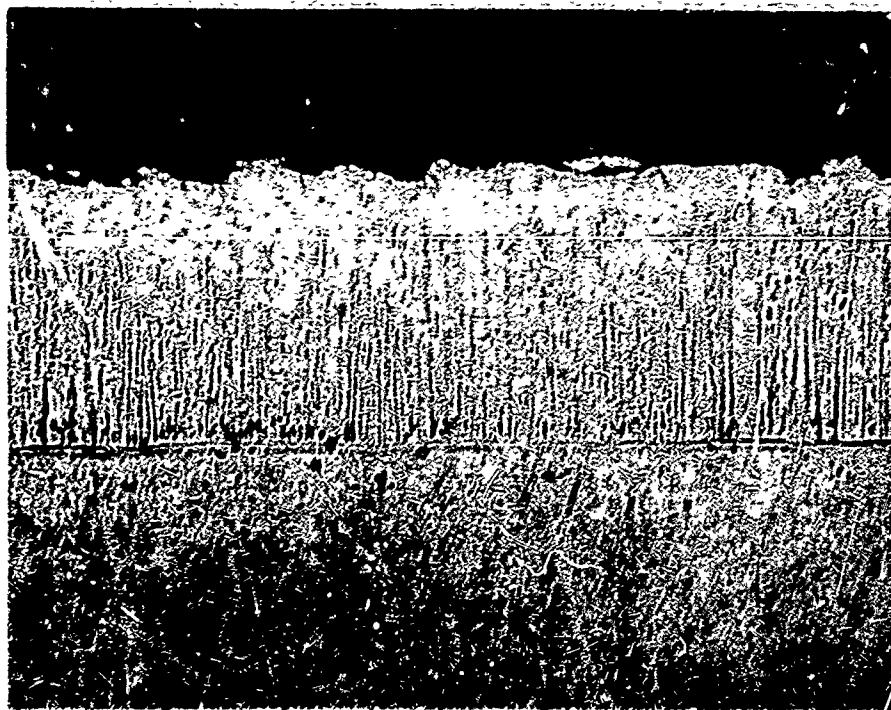
Cr-Al Second Coat Deposited at
2300°F for 16 Hours

Figure 19 - Cr-Al Second Coats on Silicide Coatings Deposited at 2100°F on Cb-1Zr (See Table 14) (250X)

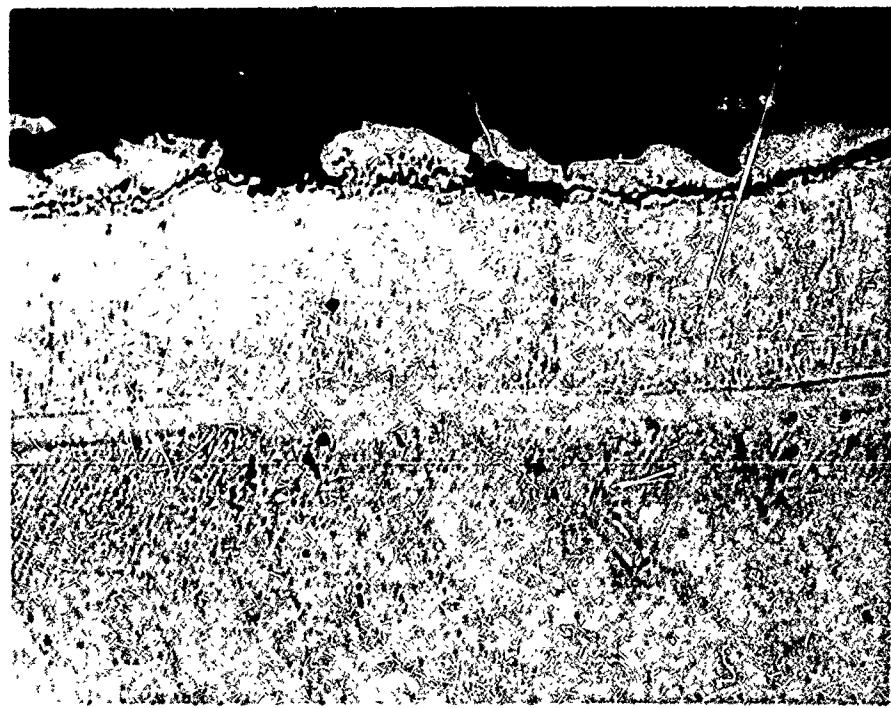


**Silicide Coating Deposited at
2100°F, Cr-Al Coating at 2300°F
for 16 Hours**

**Figure 20 - Oxidation Resistance Specimen Coated with the Si-Cr-Al System
after 10 Hours Exposure at 2600°F (See Table 14 and Figure 19)(250X)**

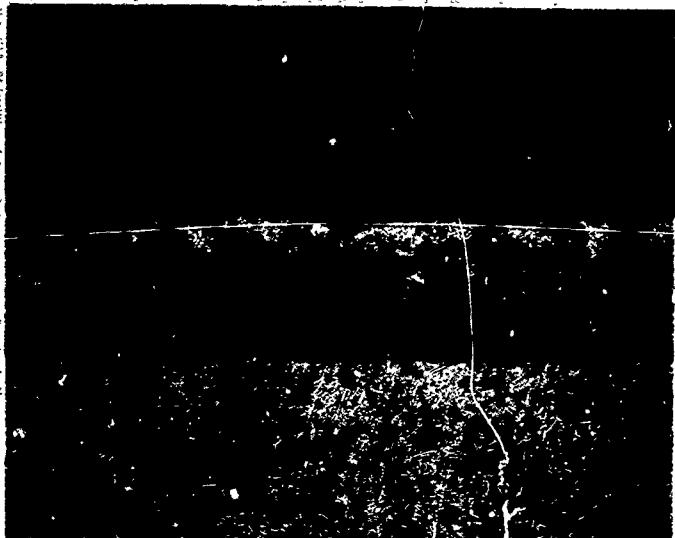


Cr-Al Second Coat Deposited at
1900°F for 16 Hours

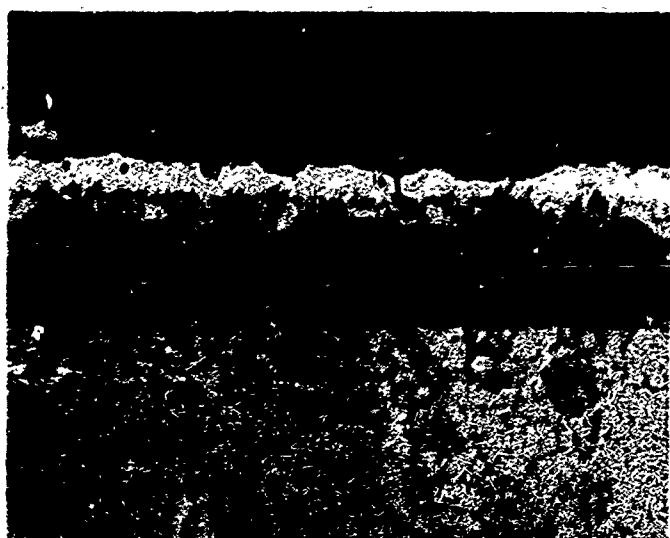


Cr-Al Second Coat Deposited at
2300°F for 16 Hours

Figure 21 - Photomicrographs of Cr-Al Second Coats on Silicide Coatings Deposited at 2300°F on Cb-1Zr (See Table 15) (250X)



(a) 1900°F - 16 Hours



(b) 2100°F - 16 Hours



(c) 2300°F - 10 Hours



(d) 2300°F - 22 Hours

Figure 22 - Cb-1 Zr Coated with Si at 1900°F for 16 Hours. Followed by Cr-B Coating at Temperatures and Times as Indicated

COATINGS FOR COLUMBIUM ALLOYS

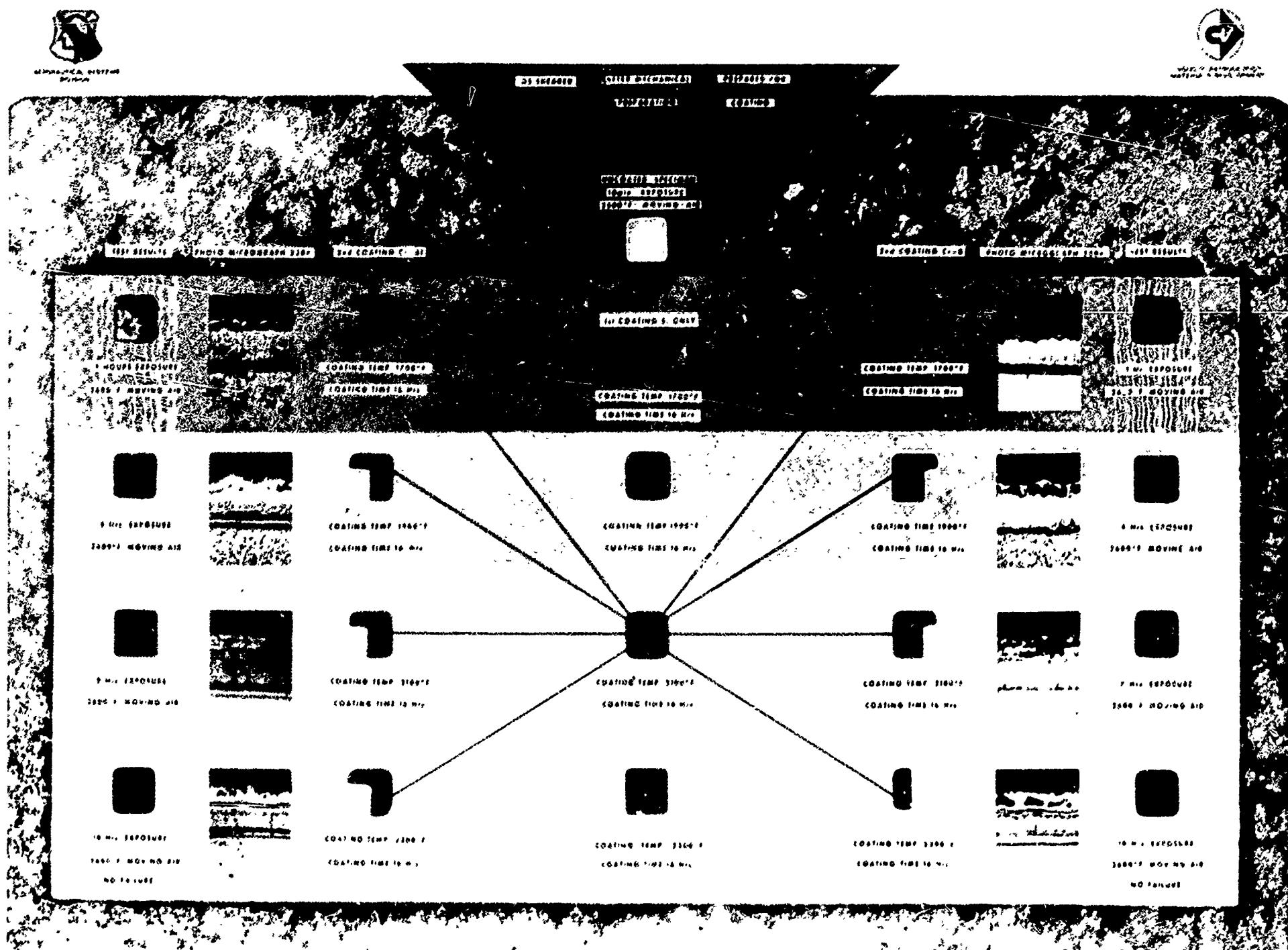
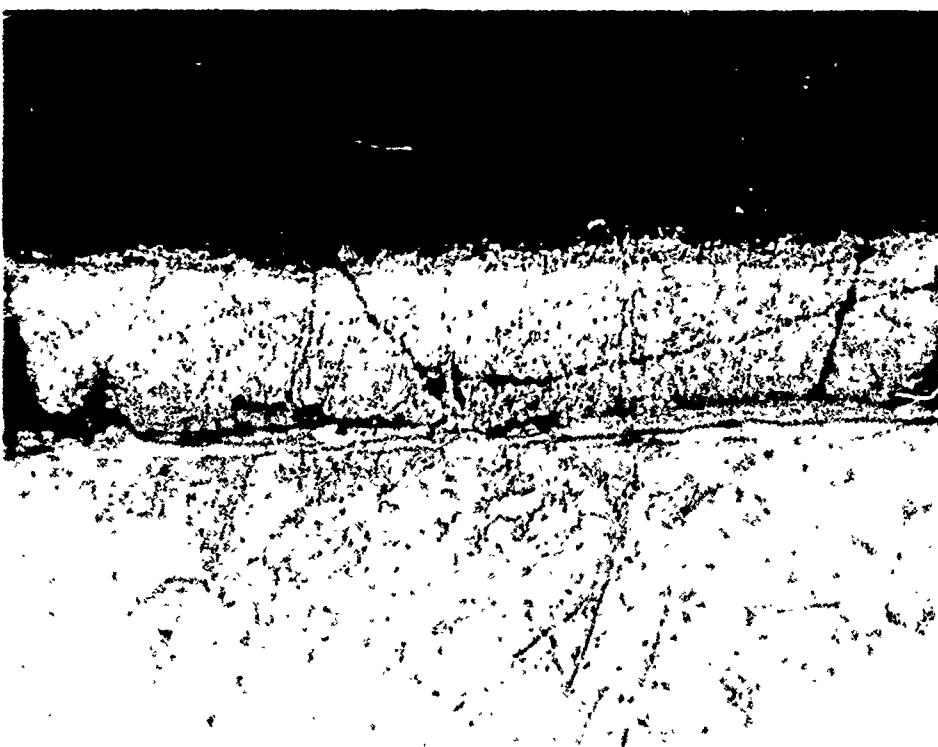


Figure 23 - Oxidation Resistance Test Specimens at Various Stages of Preparation and Testing

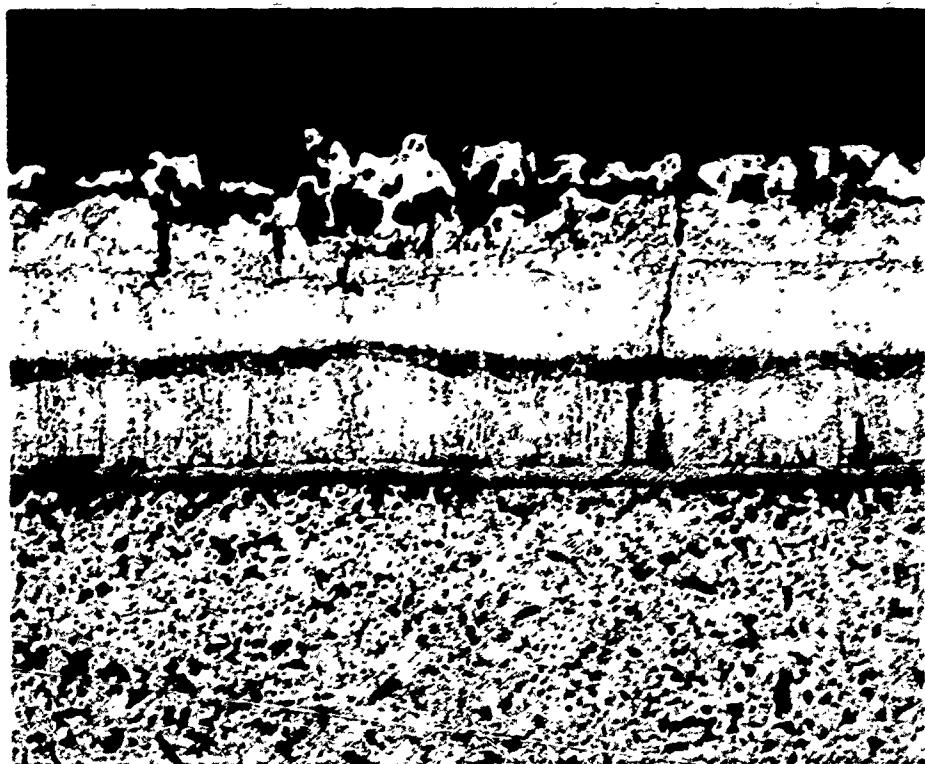


No Exposure at 2600° F



After Exposure at 2600° F for 10 Hours
Specimens Cooled to Room Temperature and Examined
after Each Hour Exposure

Figure 24 - Photomicrographs Showing Cb-1 Zr Specimens Coated with Silicide at 2100°F for 16 Hours and Cr-Al at 2200°F for 16 Hours, Tested for Oxidation Resistance at 2600°F. (250X)



Before Exposure at 2600°F



After Exposure at 2600°F for 10 Hours

Figure 25 - Photomicrographs Showing Cb-1-Zr Coated with Silicide at 2100°F for 16 Hours and Cr-B at 2200°F for 16 Hours, Tested for Oxidation Resistance at 2600°F. (250X)

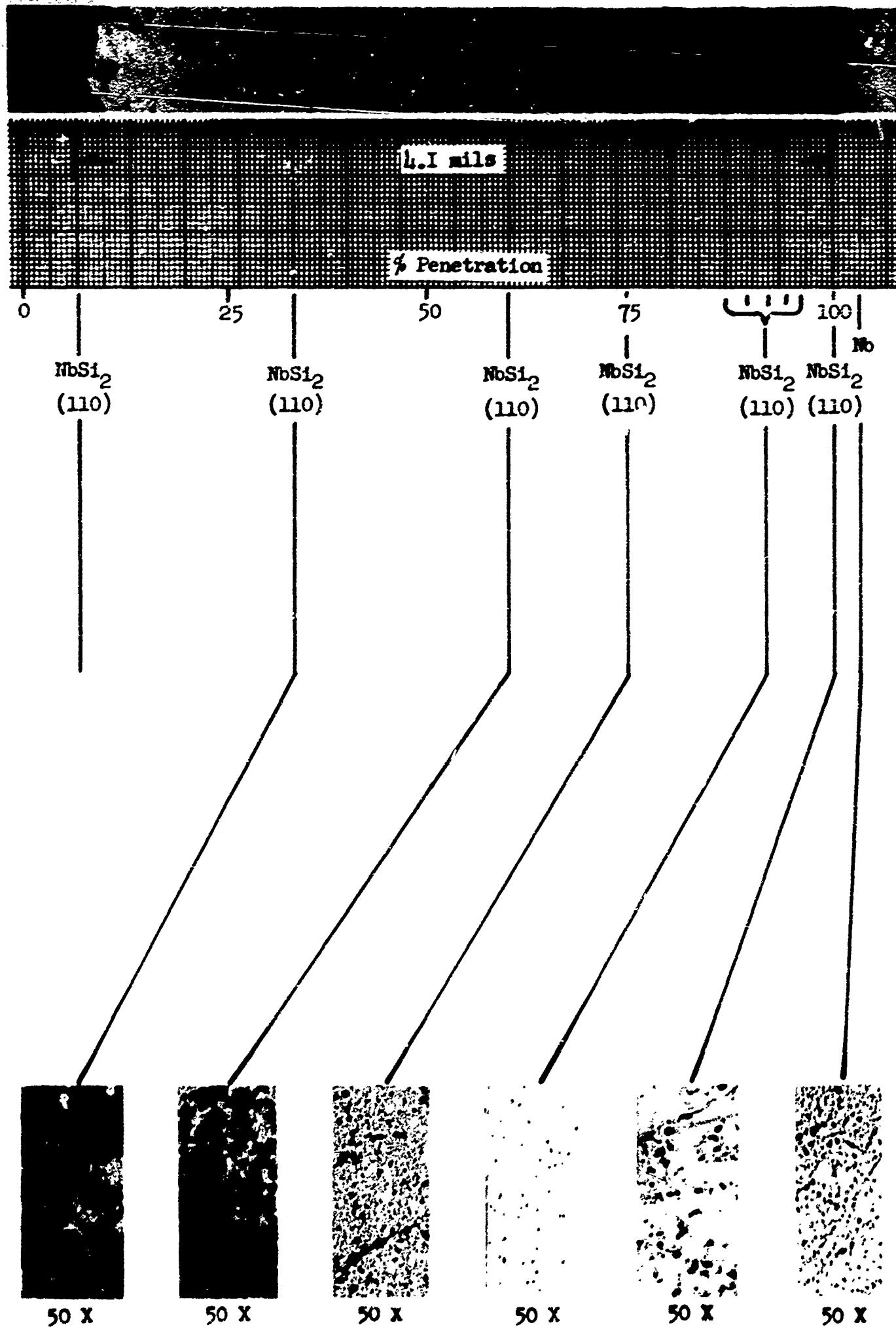


Figure 26 - Representation of Results of Analytical Evaluation
of Cb-1 Zr Coated with Silicide First Coat Only

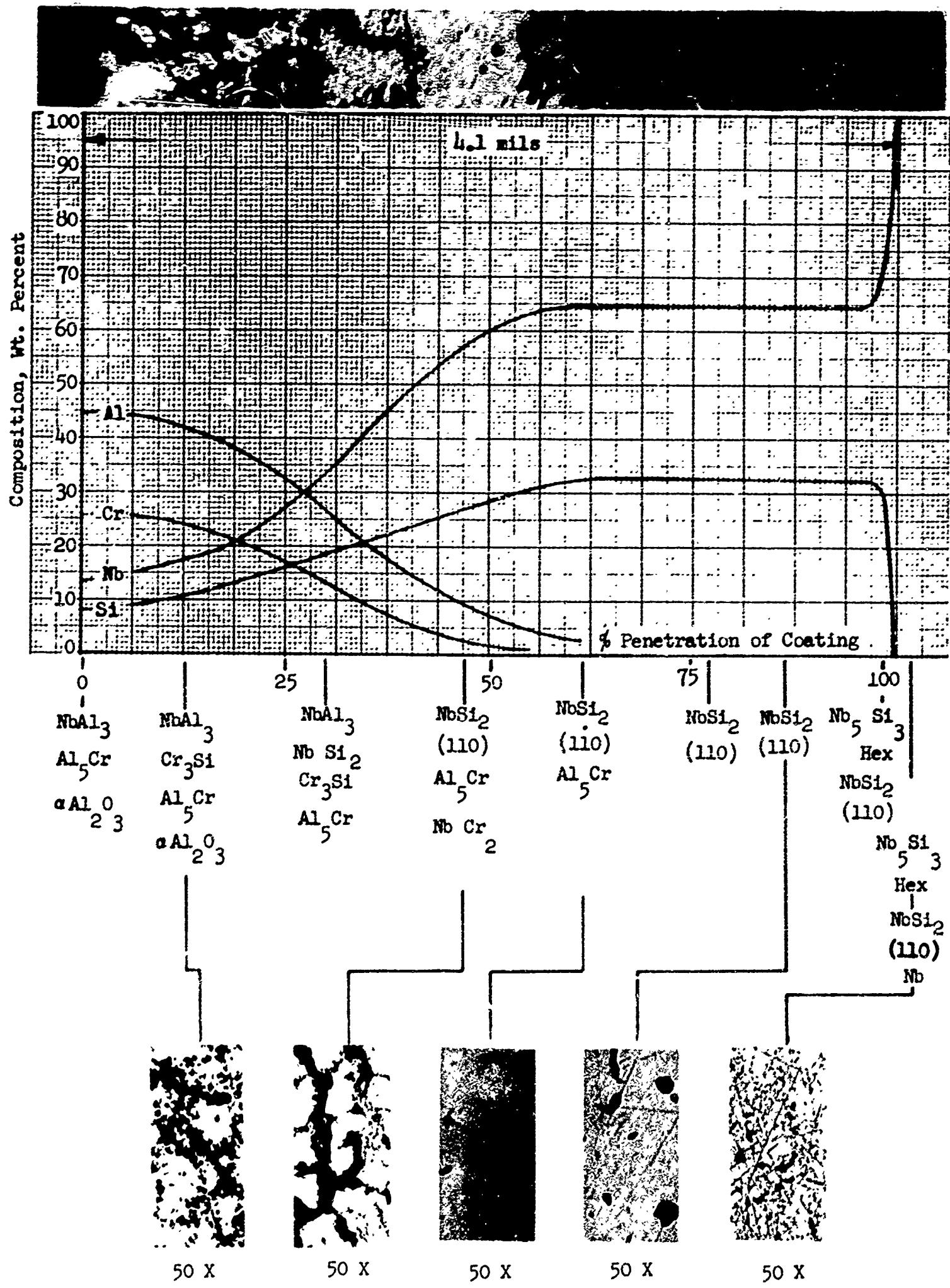


Figure 27 - Representation of Analytical Evaluation of Cb-1Zr Alloy Coated with the Si-Cr-Al System

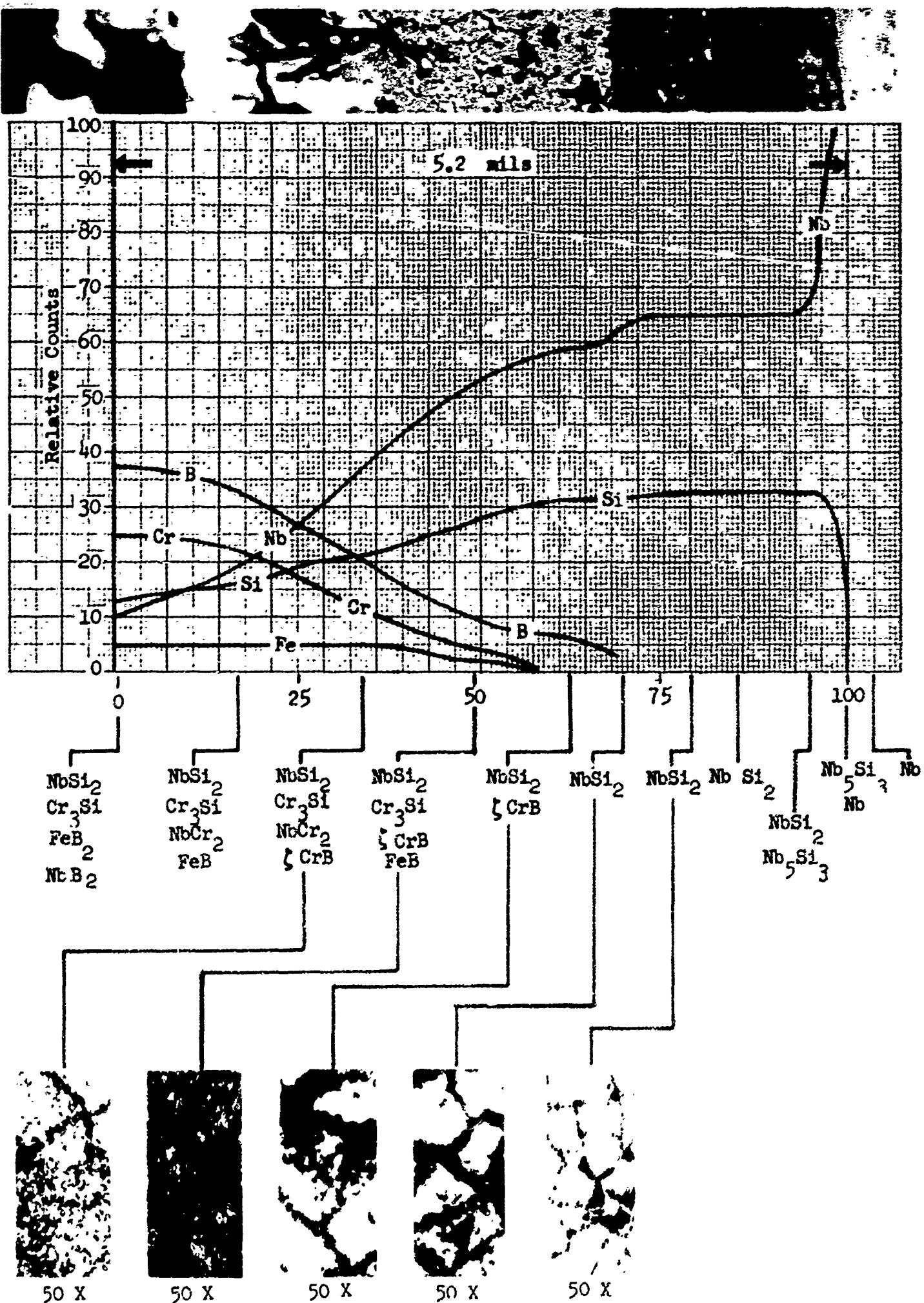


Figure 28 - Representation of Analytical Evaluation of Cb-1Zr Alloy Coated with the Si-Cr-B System

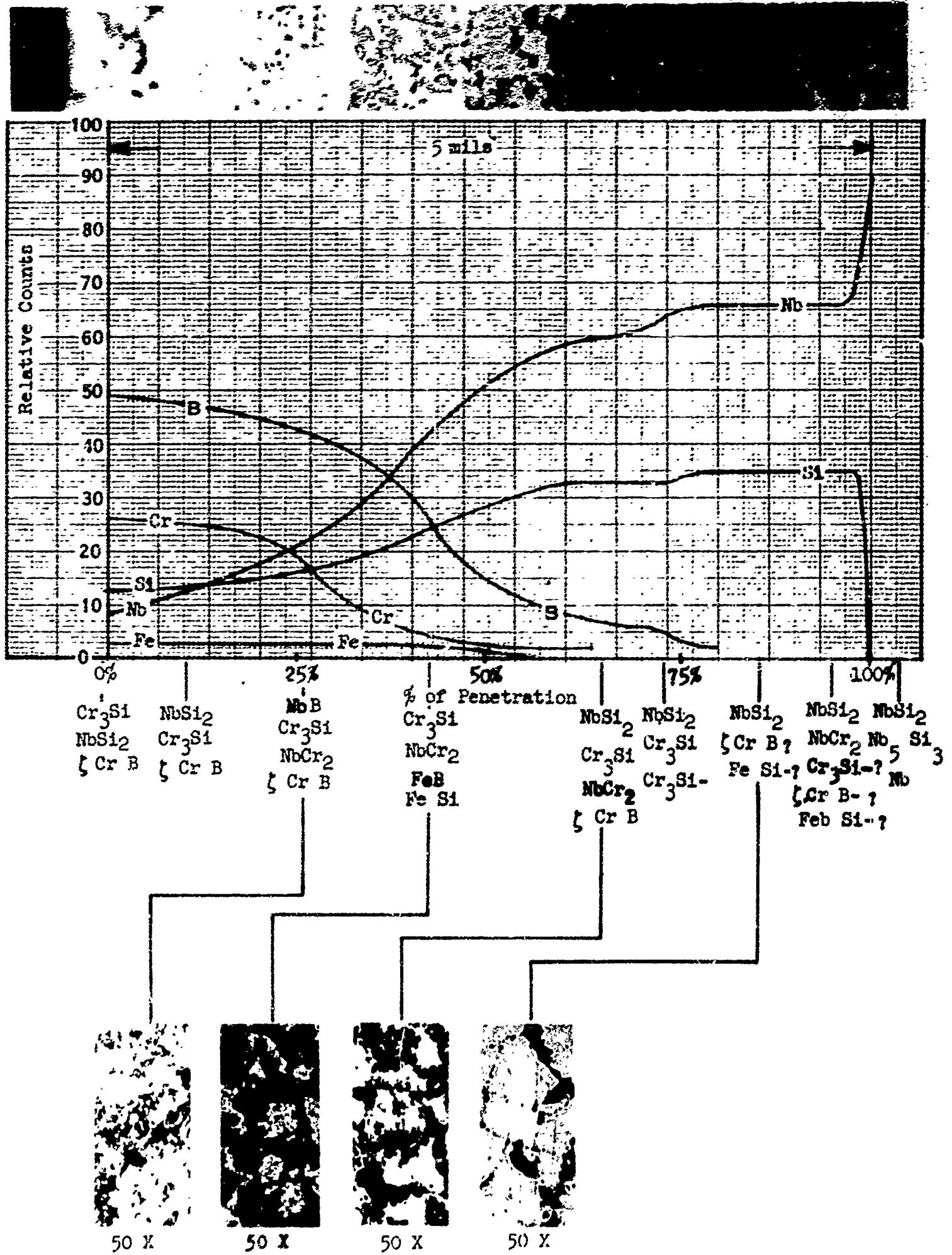


Figure 29 - Representation of Analytical Evaluation of C-103 Alloy Coated with the Si-Cr-B System

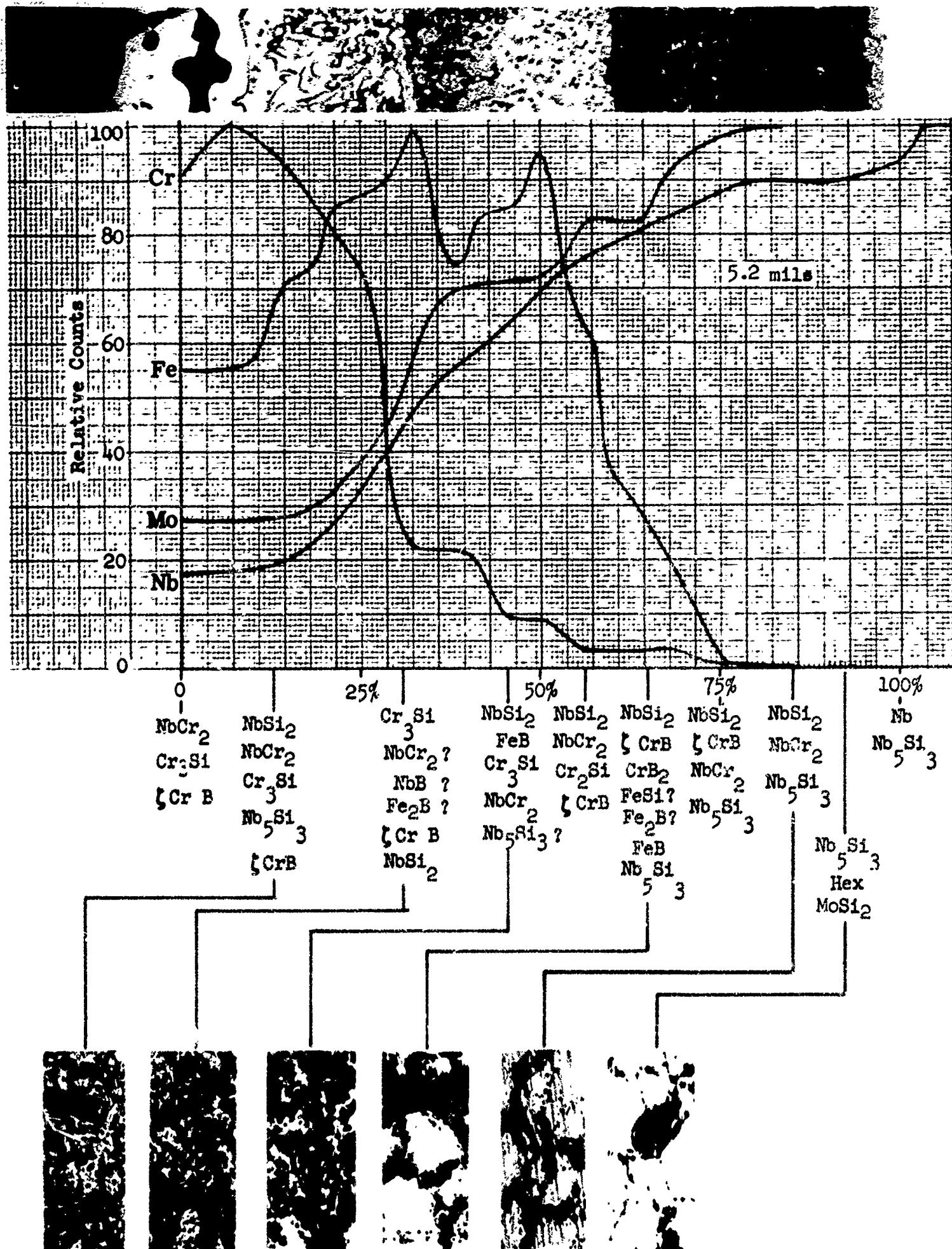


Figure 30 - Representation of Analytical Evaluation of D-31 Coated with the Si-Cr-B System

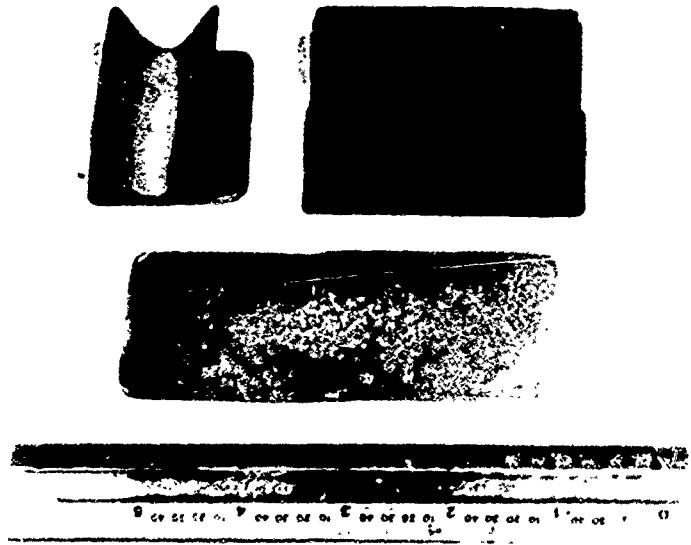


Figure 31 - Photograph Showing Welded FS-82 Alloy and Riveted D-31 Alloy Specimens Coated with the Si-Cr-B System for Oxidation Tests

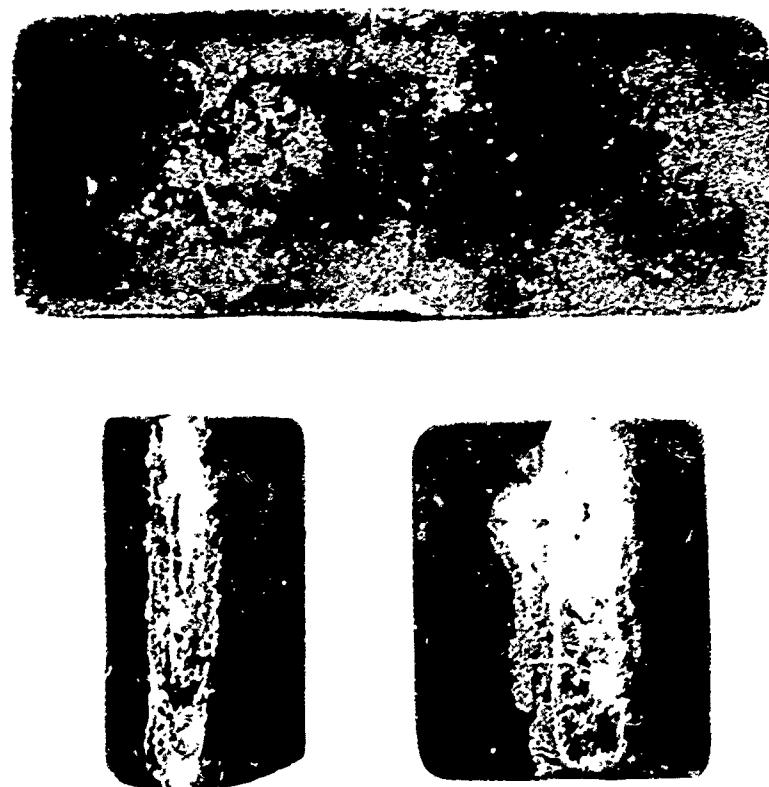


Figure 32 - Photograph Showing Lap Weld and Resistance Spot Weld Specimens after Exposure for 1 Hour at 2500°F

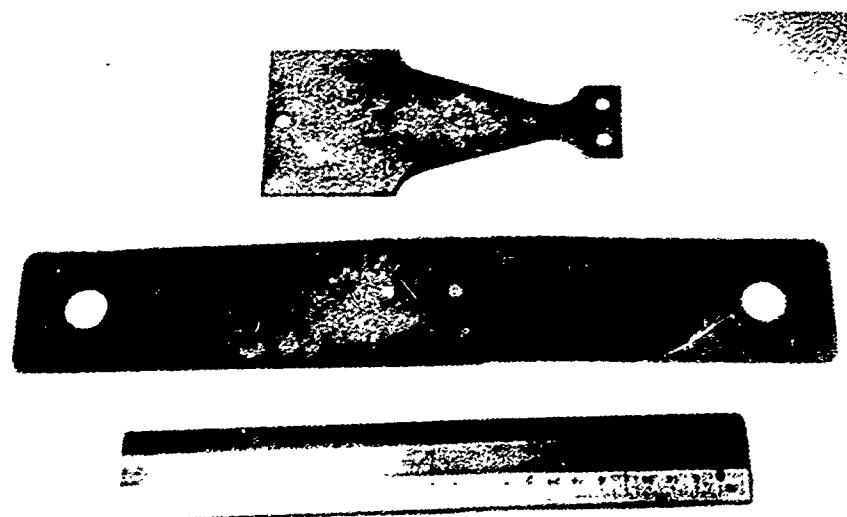


Figure 33 - Photograph Showing Cb-1Zr Alloy Lap Shear and Fatigue Specimens Coated with the Si-Cr-B System

100

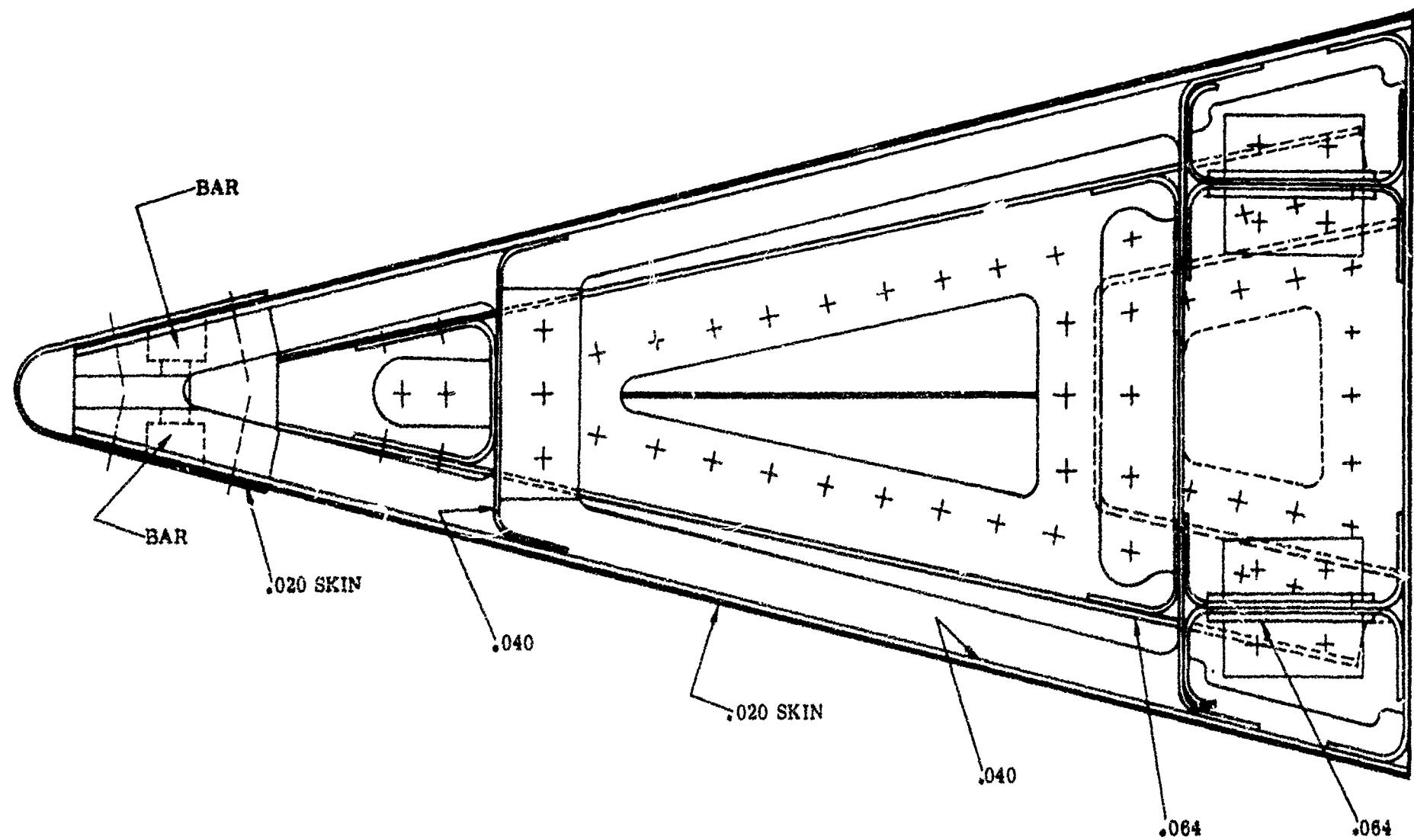


Figure 34 - Drawing of Simulated Leading Edge Assembly

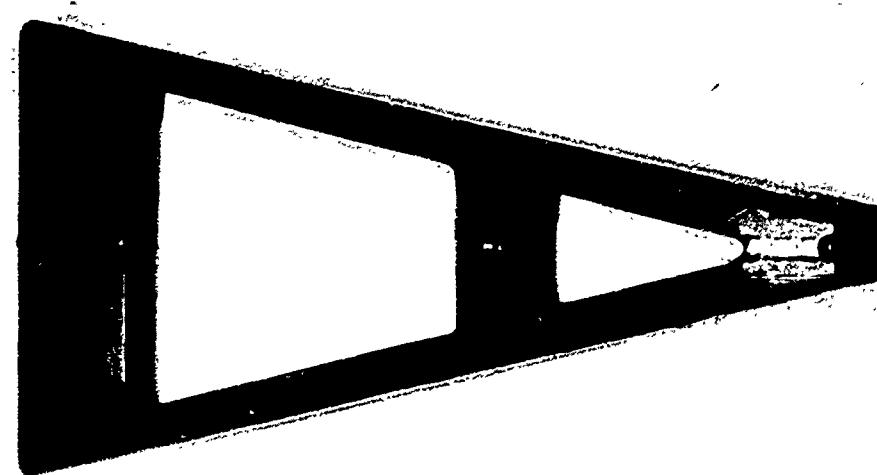
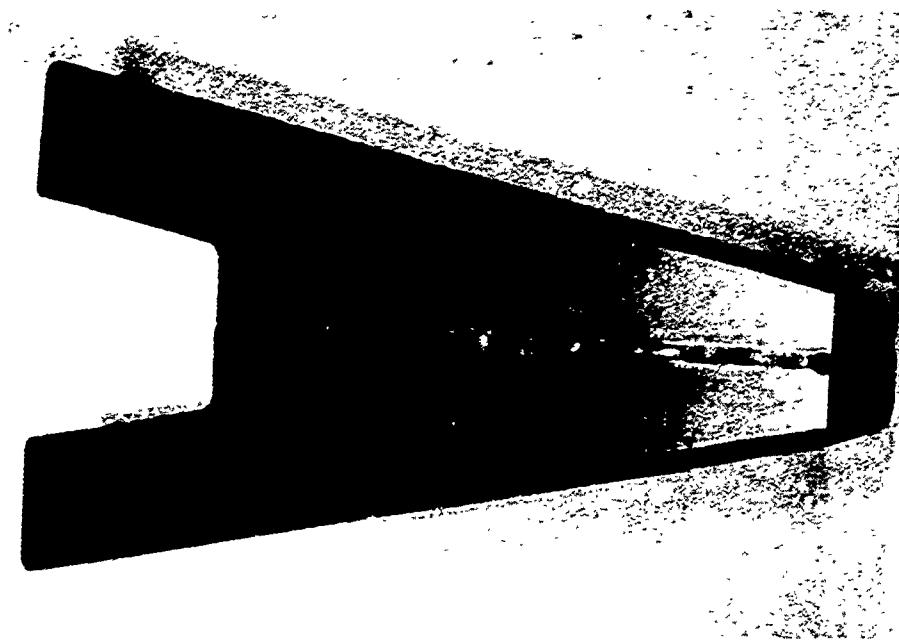
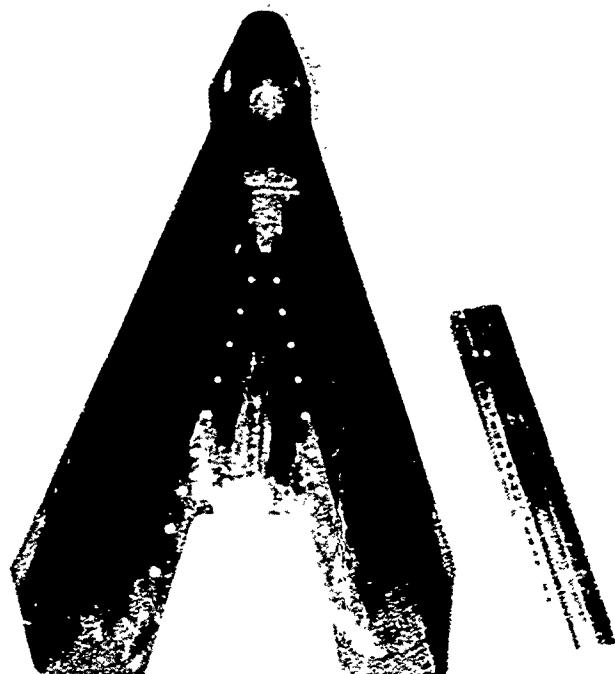
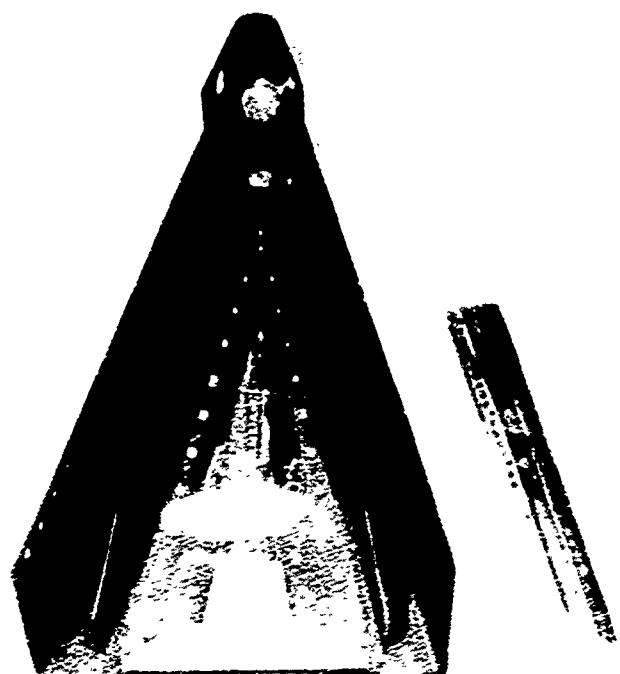


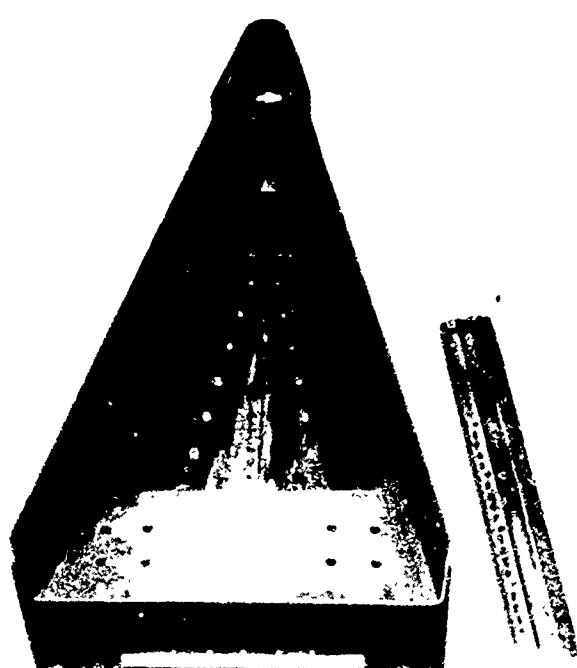
Figure 35 - Welded Components of Simulated Leading Edge Assembly



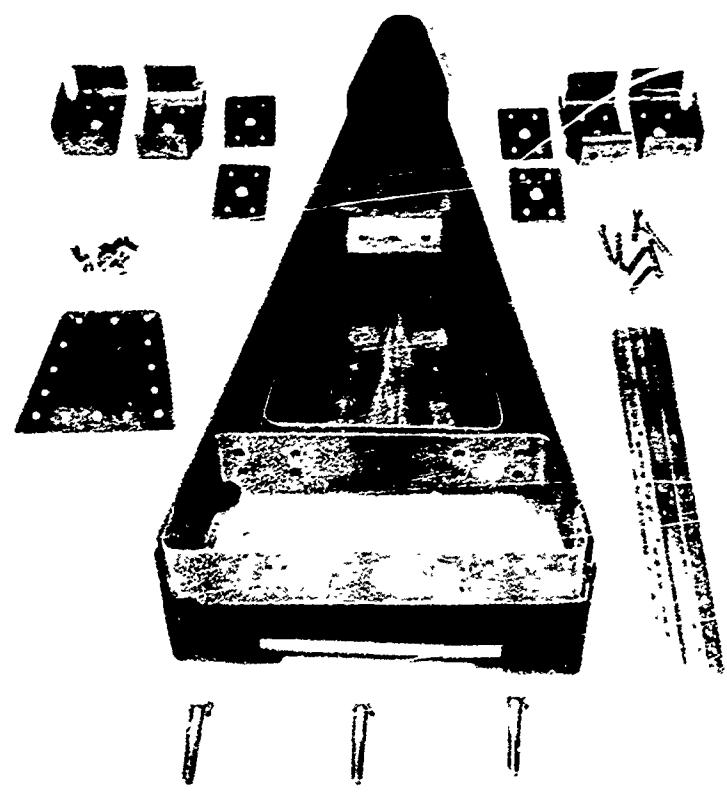
Underside of Outer Skin Surface



Outer Skin With Skin Reinforcement



Skin With Support Member for External Attachment



Complete Assembly Showing Attachment Clips, Rivets and Bolts

Figure 36 - Photographs Showing Component Parts and Sequence of Buildup of the Simulated Leading Edge Assembly

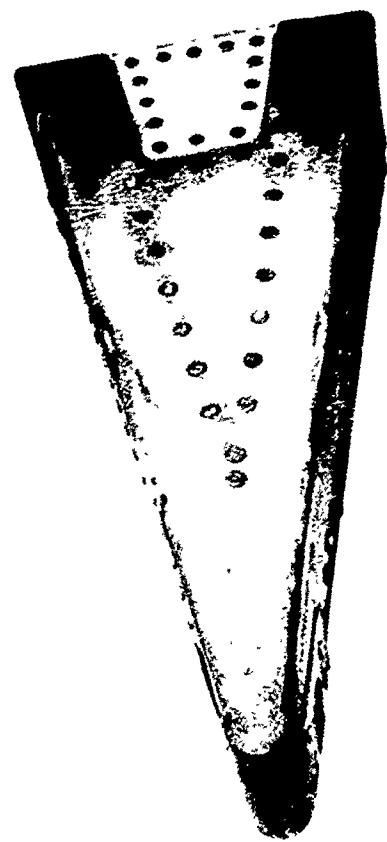


Figure 37 - Photographs Showing the Completed Simulated Leading Edge Assembly

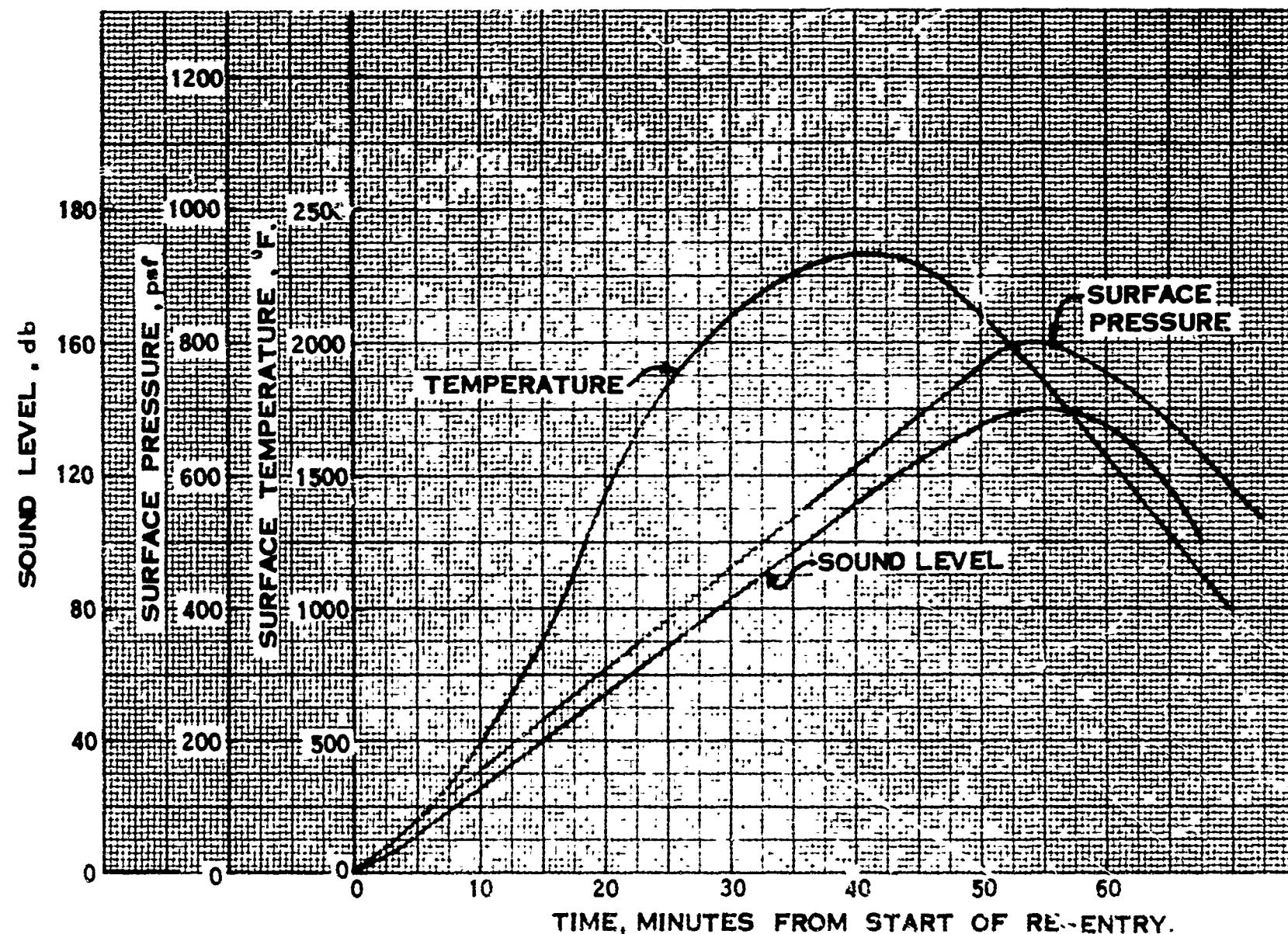


Figure 38 - Typical Re-entry Conditions for Leading Edge Surface of Glide Vehicle

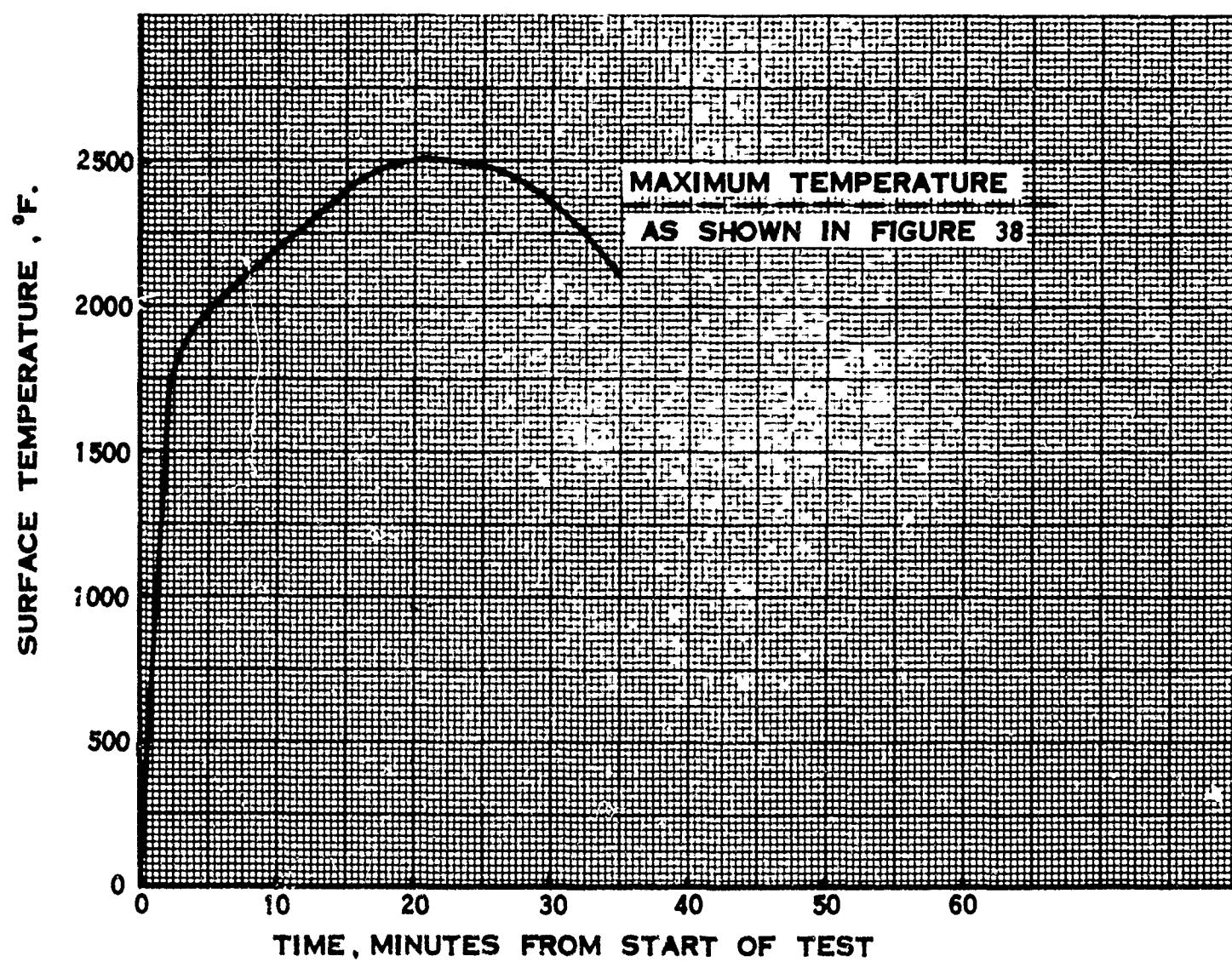


Figure 39 - Test Conditions for Simulated Leading Edge Assembly
During Propane Torch Test

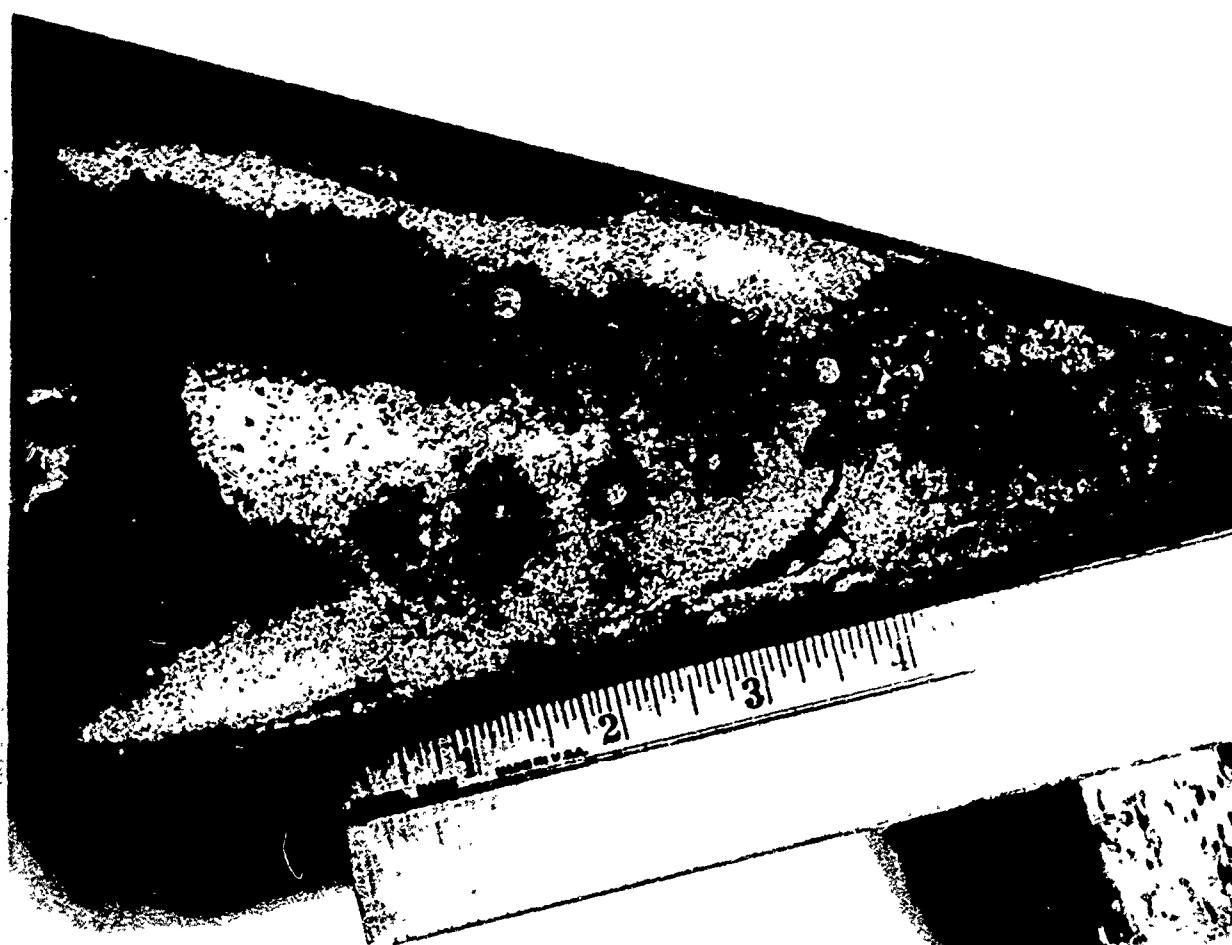


Figure 40 - Photograph Showing Top Surface of the Simulated Leading Edge Assembly after the Propane Torch Test

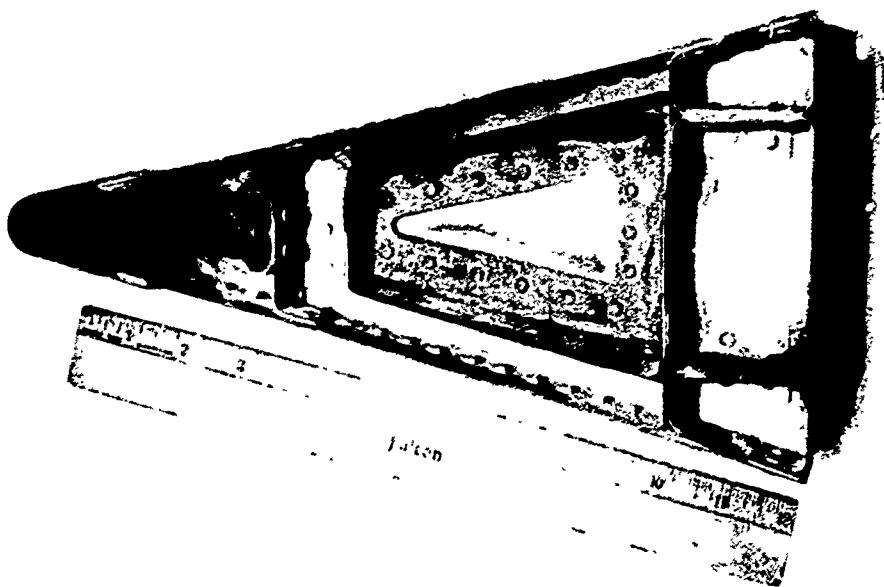


Figure 41 - Photograph Showing the Bottom Side of the Simulated Leading Edge Assembly after the Propane Torch Test

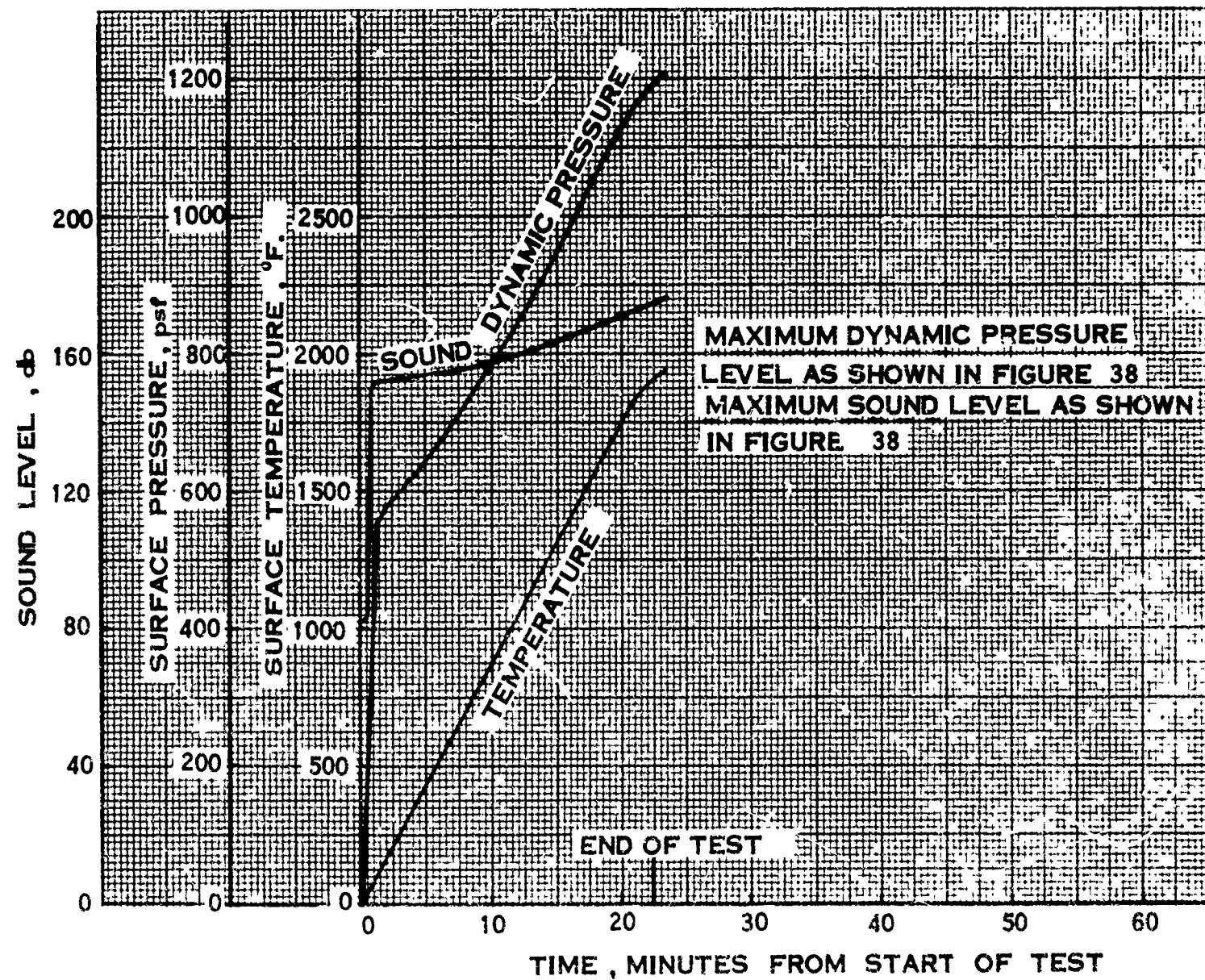


Figure 42 - Test Conditions for Simulated Leading Edge Assembly During Ram Jet Test



**Figure 43 - Photograph Showing the Simulated Leading Edge Assembly
Mounted for Test in the Ram Jet Facility**

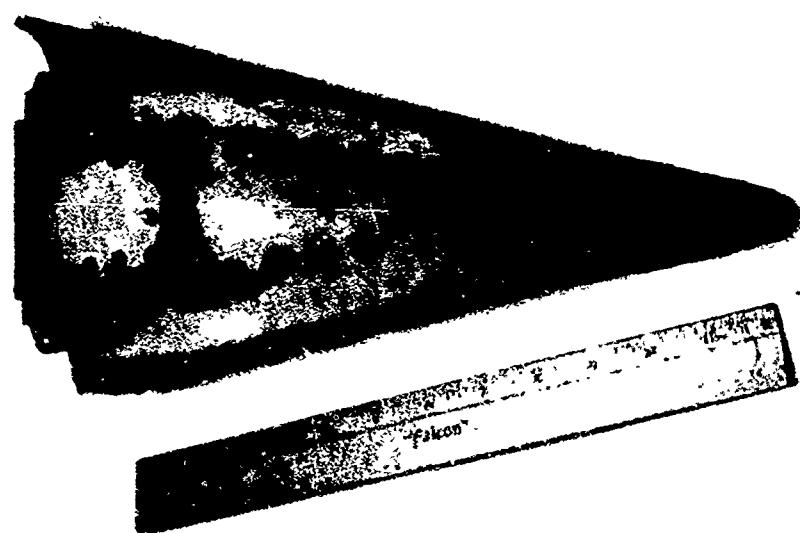


Figure 44 - Photographs Showing the Broken Portion of the Simulated Leading Edge Assembly

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